

CHARACTERIZATION AND CLASSIFICATION OF
SOME SOILS OF HAWAII WITH ANDIC AND OXIC PROPERTIES

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CHAPTER 1

INTRODUCTION

Soils which form in volcanic ash and tephra, a mixture of ash, cinders, glass, and other pyroclastic material, may be classified as Andisols. This soil order was created to recognize soils which retain the unique characteristics of volcanic ash materials. Depending on various environmental conditions, however, these materials may develop into Spodosols, Inceptisols, Mollisols, Alfisols, Ultisols, or Oxisols (Arnold, 1988).

The published soil surveys for the state of Hawaii describe 91 soil series derived from volcanic ash. These soils extend over 23% of the state and include Andisols, Oxisols, and other soil orders. The 54 series on the island of Hawaii which are formed in volcanic ash cover roughly 32% of the island (Sato et al., 1973). Of these, 52 are classified as Andepts, the precursor to the Andisol order. Nearly 20% of the soils in the state of Hawaii are currently classified as Andepts. Throughout the state, volcanic ash derived soils are used to produce sugarcane and pineapple, two of the state's major agricultural crops. Other uses of these soils include forestry, cultivation of vegetable and floral crops, and homesites.

Oxisols are also an important soil resource in Hawaii. There are 22 series mapped in the state which are

classified as Oxisols. Soils of this order cover 1.02% of the older islands of Maui, Molokai, Lanai, Oahu, and Kauai (Foote et al., 1972). They are especially important as they provide the substrate for production of sugarcane, pineapple, and pasture. As population pressure swells, these soils are being used increasingly for homesite development. Although the soil survey (Foote et al., 1972) ascribes volcanic ash parent material to only three of these series, a recent study theorizes that the soils of the Central Oahu basin were formed in, if not influenced by, volcanic ash (Gavenda, 1989).

Differentiation between Andisols and Oxisols becomes necessary in situations having the following combinations of features: 1) parent material which is basic or ultrabasic; 2) a udic or perudic soil moisture regime; and/or 3) slopes which are level or gently undulating (Kimble and Eswaran, 1988). Where this combination of properties exists in an environment, as in Hawaii, it may be difficult to distinguish the two kinds of soils on the basis of morphology alone.

In addition to similar landscape and climatic conditions, Andisols and Oxisols have some common mineralogical and chemical properties. Weathering of parent material can lead to accumulation of short-range-order minerals in both orders. In Andisols, the minerals are, however, essentially aluminosilicate in composition,

while ferric iron compounds dominate the mineral fraction of Oxisols (Kimble and Eswaran, 1988). These minerals may contribute to net positive charge on soil colloids, particularly in the case of Oxisols with low organic matter levels. The levels of acid-oxalate-extractable Al and Fe ($\text{Al}_2\text{O}_3 + 1/2 \text{Fe}_2\text{O}_3$) which are found in Andisols, may also be found in Oxisols which have undergone extreme weathering (Kimble and Eswaran, 1988). Andisols, by definition, must have a bulk density which is less than 0.9 g cm^{-3} . Except in the case of humus-rich soils, Oxisols do not have such low bulk densities. Typical bulk densities range from 1.1 to 1.2 g cm^{-3} .

Although these orders have convergent properties, the most recent revision of Soil Taxonomy (Soil Survey Staff, 1990) has provided logical places for soils of both orders (Kimble and Eswaran, 1988). Andic subgroups of Oxisols express the subordinate properties of low bulk density and high phosphorus retention. Vitrandic subgroups recognize Oxisols which contain more than 60% of volcanoclastic materials. These subgroups are known to occur in the Haploperox, Kandiperox, Hapludox, and Kandiudox great groups. Andisols with an oxic horizon within 125 cm of the surface are placed in the Oxic subgroup of the Hapludand and Haplustand great groups.

Workers in Hawaii have observed what may be a transition between the two orders. They have found soils

which retain some andic soil properties yet show development of oxic properties (Ikawa, personal communication; Gavenda, 1989). There is a need to further understand the properties of those soils with both andic and oxic characteristics, in order to manage them more efficiently for agricultural purposes. In light of the recent revisions in the soil orders of Andisols and Oxisols, there is also a need to examine the taxonomic classification of these soils.

This study will characterize the andic and oxic properties of samples of the Kolekole, Mahana, Oli, and Molokai soil series. Each of these series exhibits properties which indicate volcanic ash influence, yet each displays different magnitudes of expression of oxic properties. The hypothesis that these soils represent ash-influenced soils in various transition stages between the Andisol and Oxisol order will be tested by comparing the results of the characterization against the well-defined properties of the Akaka series (an Andisol) and the Kapaa series (an Oxisol). In addition, suggestions for revisions in the taxonomic names of these soils will be recommended as necessary.

The objectives of this study, therefore, are: (1) verify the andic and oxic properties of selected soils of Hawaii, (2) propose a methodology to group the soils with andic-oxic properties, and (3) based on the data used in this study, classify the soils with andic-oxic properties according to the revised keys to Soil Taxonomy (Soil Survey Staff, 1990).

CHAPTER 2
REVIEW OF LITERATURE
Andisols

Central Concepts of the Andisol Order

The Andisol soil order is intended to classify soils derived from volcanic ejecta (such as volcanic ash, pumice, or cinders), and/or volcanoclastic materials, which appear to have weathered beyond mere accumulation of raw parent material, yet retain certain properties of volcanic soil materials. These properties can include low bulk density, high specific surface area, variable charge characteristics, accumulation of organic carbon, development of Al-humus complexes and high phosphate retention. Water retention, at both 1500 kPa and 33 kPa, is high relative to soils of comparable texture (Wada, 1985). While slightly weathered particles of volcanic glass may be dominant in some places (Arnold, 1988), generally the extent of weathering has been such that the mineralogy of the colloidal fraction is dominated by short-range-order minerals such as allophane, imogolite and ferrihydrite, or Al-humus complexes (Leamy and Kinloch, 1988).

Some soils having short-range-order minerals of apparently non-volcanic origin are also included in Andisols on the basis of their properties (Leamy and

Kinloch, 1988). The soil pedons show minimal profile development.

The Andisol order has only recently been recognized. Soils of volcanic ash origin were initially placed in the Inceptisol order, under the suborder Andept. Inceptisols were originally conceived of as rather weakly weathered soils. According to Dr. Guy Smith, it was "more or less a wastebasket order for the soils that did not fit any of the other nine orders," (Smith, 1986). The original concept of the Andepts was developed in Japan by researchers working with the Korobuco (sic) soils; these volcanic ash-derived soils have very dark colors and are very high in their percentage of organic matter (Smith, 1986). Their A horizons are thick and dark-colored, reflecting the amount and optical properties of the humic acids produced by the decomposing organic matter (Arai et al., 1988).

The Soil Taxonomy (1975) recognized Andepts as "more or less freely drained Inceptisols that have low bulk density ($< 0.85 \text{ g cm}^{-3}$) and have an appreciable amount of allophane that has a high exchange capacity or that are mostly pyroclastic materials (e.g. $> 60\%$ vitric volcanic ash, cinders, or other vitric pyroclastic material)." Pyroclastic, sedimentary, or basic extrusive igneous rocks were recognized as parent materials, along with volcanic ash. Seven great groups were recognized under the

suborder Andepts (Soil Survey Staff, 1975). Only five of these, the Eutrandepts, Dystrandepts, Hydrandepts, Placandepts, and Vitrandepts have been mapped in Hawaii.

As research on volcanic ash-derived soils progressed, it became apparent to soil scientists that the Andept suborder was deficient in many ways. The suborder did not satisfactorily deal with soil climate, base saturation, soil color, mineralogy, and particle size class.

Dr. Guy Smith was among the first to perceive these inadequacies. While working in the volcanic islands of the West Indies, and later on the North Island of New Zealand, Smith found that he was unable to make interpretations regarding proper use of the soil without a great deal of information that was not included in the family name. During his stay in New Zealand, Dr. Smith devised a proposal, first presented in 1978, which would establish an eleventh order, the Andisols (Smith, 1986).

An international committee of soil scientists (ICOMAND) has been evaluating this proposal since its initial presentation. They have established standard requirements which have been accepted by the Soil Conservation Service as the latest amendment to the Soil Taxonomy (Soil Survey Staff, 1990). The new order uses soil moisture and temperature regimes to distinguish between suborders, and defines a new set of particle size classes for soils from pyroclastic materials. Soil color

is an identifying characteristic for the Thaptic subgroups, and the Melan- and Fulv- great groups. In addition, total bases are substituted for base saturation as a criterion for classifying the Eutric subgroups.

Definition of Andisols

Andisols have been defined as soils which "have andic soil properties throughout subhorizons, whether buried or not, which have a cumulative thickness of 35 cm or more within 60 cm of the mineral soil surface or upper boundary of an organic layer that meets andic soil properties, whichever is shallower," (Soil Survey Staff, 1990).

According to Keys to Soil Taxonomy (Soil Survey Staff, 1990), soil material with andic properties must have less than 25 percent organic carbon and have 2.0 percent or more acid-oxalate-extractable aluminum plus $1/2$ acid-oxalate-extractable iron ($Al_0 + 1/2Fe_0$) in the less than 2.0-mm fraction. In addition, the bulk density of the less than 2.0-mm fraction, when measured at 33 kPa water retention, must be 0.90 g cm^{-3} or less. Finally, phosphate retention of the less than 2.0-mm fraction, when measured by the New Zealand method (Blakemore et al., 1987), must be 85 percent or more.

Exceptions to this last requirement are allowed for Andisols which contain volcanic glass. If the phosphate retention of the less than 2.0-mm fraction is more than 25 percent and the 0.02 to 2.0-mm fraction is at least 30 percent of the less than 2.0-mm fraction, then the $Al_2O_3 + 1/2Fe_2O_3$ may vary between 0.4 and 2.0 percent (Soil Survey Staff, 1990).

This definition of the order allows any kind of diagnostic epipedon, provided minimum requirements are met in and/or below the epipedon. In addition, any kind of diagnostic horizon is allowed below the 35-cm layer which exhibits minimum expression of andic soil properties required for the order (Leamy, 1988). Usually the Andisols exhibit an umbric or ochric epipedon and a cambic horizon; a mollic epipedon and a cambic horizon may be seen in some cases (Wada, 1985).

Andisols may be differentiated from Entisols by the degree of weathering. In Andisols, the minimum acceptable degree of weathering is expressed as percent of $Al_2O_3 + 1/2Fe_2O_3$. This value corresponds to of a minimum amount of short-range-order materials (Leamy, 1988). Immature andic soils, primarily Vitrandis, may be the Andisol member of the Andisol-Entisol transition. The two may be distinguished by the thickness of the andic layer (Amano, 1988).

The nature of the weathering product differentiates Andisols from Inceptisols. This product is dominantly short-range-order minerals in Andisols, rather than the crystalline clay minerals found in Inceptisols (Leamy, 1988).

Although the presence of albic and/or spodic horizons is typical of Spodosols, these diagnostic horizons may also occur in Andisols. In many cases, distinction between Andisols and Spodosols may be made based on the presence of andic soil properties in the former order and the absence of these properties in the latter order. Spodosols often develop under forest vegetation and in humid climates. For volcanic ash-derived soils in forested regions, distinction between the Andisols and Spodosols is dependent on the thickness of the soil materials which meet requirements for andic soil materials and the depth to these materials.

Finally, Andisols may be differentiated from Oxisols because horizons with andic soil properties commonly contain an appreciable quantity of weatherable minerals. Also, oxic horizons do not commonly contain allophane or Al-humus in significant amounts (Leamy, 1988). The Oxisol and Andisol orders have many convergent properties and distinction between the two, if based on morphology alone, is not always easy. This issue will be discussed later in this study.

The revisions to the Soil Taxonomy which established the Andisol order have made necessary revisions to the classifications of the Andepts in Hawaii. A review of recent literature (Kinloch et al., 1988) reveals the reclassification of several soil series in Hawaii as Andisols. Table 2.1 lists these series and their current Andisol great group, along with the Andept great group in which they were formerly classified.

Table 2.1. Soil series classified as Andisols.

Soil Series	Andisol	Great Group	Andept ^e
Akaka	Hydrudand ⁺		Hydrandept
Apakuie	Haplustand [*]		Vitrandept
Hilo	Hydrudand ⁺		Hydrandept
Kaipoi	Haplustand ⁺		Dystrandept
Kikoni	Haplustand [*]		Eutrandept
Kilohana	Vitrand [*]		Vitrandept
Kula	Haplustand ⁺		Eutrandept
Kukaiau	Hydrudand ⁺		Dystrandept
Maile	Hapludand ⁺		Dystrandept
Niulii	Hapludand ⁺		Dystrandept
Olinda	Hapludand ⁺		Dystrandept
Pane	Haplustand ⁺		Dystrandept
Waimea	Haplustand ⁺		Eutrandept

^e Source: Foote et al., 1972; Sato et al., 1973

⁺ Source: Kinloch et al., 1988.

^{*} Source: Ikawa, Sato, and Chu, 1988.

Selected Physical Properties of Andisols

Andisols show many unique physical properties; these include low bulk density, high porosity, smeary consistency, and high water retention values. In addition, Andisols are normally permeable, with a high rate of percolation, and form very stable aggregates. Factors such as particle-size distribution, organic matter content, and geologic history affect the physical and engineering properties of these soils. The charge characteristics of the clay fraction, the shape and size of unit particles, and the way these particles form secondary aggregates have also been identified as major factors controlling these properties (Wada, 1989).

By definition, Andisols have bulk densities less than 0.90 g cm^{-3} (Soil Survey Staff, 1990). The low bulk density is partly due to high humus contents; the particle density of humus is generally 1.4 to 1.8 g cm^{-3} . The low particle density of volcanic glass, 2.4 g cm^{-3} (Wada and Wada, 1977) is also partly responsible. The low bulk density mainly reflects the high porosity of these soils (Wada, 1985).

Andisols have small to very small volumes of solids and large volumes of pores. The proportions of water and air in the pores vary widely. The small volume of solids may pose a problem for the supply and retention of plant nutrients. In contrast, the large pore volume

ensures aeration, water permeability, and retention. Allophane and imogolite have 25 to 45 percent pore space in their structural units. This fact partly accounts for the large pore space of Andisols containing these minerals (Wada, 1985). Soils containing considerable amounts of humus also have high porosity. These relationships suggest that the micro pores are present as intra-unit pores in allophane, imogolite, and Al-humus complexes, while the medium to micro pores are created by interactions between them and other clay-silt, and sand-sized minerals, resulting in formation of stable aggregates (Wada, 1985, 1989). In this aggregate formation, polymer hydroxy-Al ions and allophane, allophane-like constituents and imogolite, which carry positive charge and contain active Al, play an important role.

A high water content measured at 33 kPa suction is a common feature of Andisols. In dry parts of Hawaii, 20 to 70 percent of the water percentage measured at 33 kPa suction and higher is available, although the actual 33 kPa water content varies widely. Hydrandeps in the perhumid regions of Hawaii are high in 33 kPa water, but only a portion of this water, ranging from 15 to 30 percent, may be available (Wada, 1985). This feature may indicate the role of non-crystalline Al- and Fe-hydroxides rather than allophane and imogolite (Wada, 1985).

As inferred above, high water contents at 1500 kPa are also typical of Andisols. This feature may be related to the presence of micropores within and between the allophane unit particles. When close-packed, these particles can retain 400 to 800 g kg⁻¹ water in those micropores (Wada, 1989).

Soils having a high allophane and imogolite content have high liquid and plastic-limit values and show slippery or smeary consistency but are non-sticky. Undried allophanic soils do not show a distinct maximum in bulk density on compaction (Wada, 1985). Although no longer used in the taxonomy as a modifier for particle-size class, the term "thixotropic" is commonly used by soil scientists in describing these soils. A thixotropic soil has the capacity to pass from a solid state to a liquid or gel-like state upon agitation (Plaisance and Cailleux, 1981). This quality is characteristic of the Hydrandepts and Hydric Dystrandepts of the former classification system.

Although the soils have high amounts of percolation, the profiles show no evidence of clay movement. This lack of eluviation is an indicator of the stability of the aggregates formed by reactions between the inorganic constituents and humus. These aggregates are stable in an undisturbed state and are relatively resistant to erosion. In the laboratory, these aggregates are disrupted by

treatment with hydrogen peroxide and sonic oscillation. Adjustment of the pH and sonic vibration are important for deflocculation and dispersion after the hydrogen peroxide treatment (Wada, 1985).

The natural water content of some allophanic soils is close to their liquid-limit values (Wada, 1989). Thus, they are sensitive to mechanical disturbance and show very little strength after being disturbed. In spite of their natural high water content, the soils have a high load bearing capacity before disturbance. Their unconfined compressive strength is in the range of 1.0 to 2.3 kg cm^{-2} . This value is more than five times the strength of alluvial soils at the same water content (Wada, 1985).

Chemical Properties of Andisols

The variable charge characteristics of Andisols are a great challenge for management of soils for agriculture. Soils with variable charge are those soils whose negative charge increases with pH and whose positive charge, if present, decreases with pH. In addition to pH, the nature and concentration of cations and anions in solution and temperature influence the development of variable charge (Wada, 1989). These characteristics influence ion exchange, base saturation, and adsorption of both cations and anions. Variable charge is also a factor in structure development (Wada, 1989).

The variable charge in Andisols arises from sites on soil organic matter, allophane, and iron oxides. Minerals such as halloysite, interlayered vermiculite, or other layer silicate minerals which may be present in some Andisols have negative charge which does not vary greatly with pH (Wada, 1980).

The negative charge or cation exchange capacity (CEC) of soil organic matter increases with pH and may significantly increase the net charge of a soil. Both the amount and type of organic matter are important in this reaction. For example, a soil containing 10% allophane will carry 1 meq/100 g of positive charge at pH 5 and 1 meq/100 g of negative charge at pH 7. If the same soil also contains 10% organic matter, it will have a net charge (CEC) at pH 7 of 31 meq/100 g. The organic matter contributes 30 meq/100 g of negative charge while the allophane contributes only 1 meq/100 g (Parfitt, 1988).

Positive charge arises in allophane when the $\text{AlOH}(\text{H}_2\text{O})$ groups at its surface react with H^+ ions. When the same groups react with OH^- ions, negative charge arises (Parfitt, 1988). Anion exchange capacity develops under conditions of positive charge while cation exchange capacity develops under conditions of negative charge. Allophanic A horizons or A horizons rich in Al-humus complexes seldom have any positively charged sites (Wada and Okamura, 1980). Some allophanic B horizons, however,

have up to 10 meq/100 g positive sites at pH 5 and up to 5 meq/100 g at pH 6 (Wada 1980).

A positive delta pH, (i.e., $\text{pH}[\text{KCl}] - \text{pH}[\text{H}_2\text{O}] > 0$) indicates the presence of net positive charge. Positive delta pH values on the ICOMAND Database are observed for four Hydroperand B horizons from Fiji and Hawaii (Parfitt, 1988). Many of these horizons have considerable amounts of ferrihydrite or hematite which could contribute to the positive charge.

The FeOH groups of ferrihydrite, can acquire positive or negative charge in a similar manner to the AlOH groups of allophane (Schwertmann and Fechter, 1982). It was found that 90% of the 1,017 Andisol horizons in the ICOMAND database had less than 5% ferrihydrite, as estimated by $1.7 \times$ acid-oxalate-extractable Fe (Childs, 1985, cited in Parfitt, 1988). Ferrihydrite contents of more than 10% were found in soils formed in basaltic tephra under high rainfall in Hawaii and Fiji. Most Andisols, however, contain less ferrihydrite than allophane.

Allophane and/or ferrihydrite, if present in large amounts relative to organic matter, may contribute significantly to the variable negative charge (Parfitt, 1988; Wada, 1980). The type of allophane, as defined by the Al/Si ratio, may be related to this effect. Soils with allophane having $\text{Al/Si} = 1$ have more negative charge

at a given pH than soils with allophane having $Al/Si = 2$ (Wada, 1980). Thus, the range of effective cation exchange capacity (ECEC) values at a given pH, for the allophanic A horizons mentioned previously, appears to be related not only to the amount and type of humus but also to the amount and type of allophane present (Parfitt, 1988).

Some Fiji soils, formed in recent basaltic tephra, have a sum of cations ($Ca + Mg + K + Na$) as high as 60 meq/100 g (Parfitt, 1988). In over half of the Andisol A horizons in the ICOMAND database, the sum of cations is less than 10 meq/100 g (Parfitt, 1988). These low values may arise in soils with low pH and low levels of organic carbon.

The adsorption of such heavy metal cations as Co, Ni, Cd, Zn, Cu and Pb is important from both agricultural and environmental standpoints. A higher proportion of the cation-exchange sites on allophane and imogolite exhibit higher selectivities for metal cations as compared with smectites (Wada, 1989).

The phosphate anion can sorb on both positively and negatively charged surfaces containing $AlOH$ and $FeOH$ groups. This reaction involves ligand exchange of phosphate anions with the OH^- groups (Parfitt, 1980; Barrow, 1985, cited in Parfitt, 1988). Analysis of the ICOMAND database showed that most Andisol B horizons have

large phosphate retention capacities, presumably because of the presence of allophane and iron oxides (Parfitt, 1988). Also, approximately two thirds of the Andisol A horizons have phosphate retention values greater than 85 percent.

The sulfate anion can also be retained by sorption on the surfaces of allophane and iron oxides (Bohn et al., 1986, cited in Parfitt, 1988). Sulfate is less strongly sorbed than phosphate and sulfate sorption decreases markedly as pH increases. Parfitt's analysis of 177 Andisol B horizons showed that many of these horizons have high levels of sorbed sulfate (1988).

Oxisols

Central Concepts of the Oxisol Order

The Oxisol soil order describes soils which have undergone intensive weathering. The result is soils which are composed primarily of clay and sand, with a low percentage of weatherable minerals. They are high in crystalline oxides and hydroxides of Fe and Al, and in some cases, Ti. The dominant alumino-silicate clay mineral is kaolinite. Only very low amounts of 2:1 layer silicate clays are present, if any. Other minerals which are commonly present in Oxisols are gibbsite, hematite, goethite, anatase, and rutile (van Wambeke et al., 1983).

Chemically, these soils are identified by variable charge characteristics and very low cation exchange capacity (CEC) per unit clay (Fanning and Fanning, 1989). These soils, furthermore, are generally red in color with hues ranging from 7.5YR to 10R and have gradual or diffuse boundaries between horizons.

Large areas of old reworked sediments which have been deposited on stable surfaces and/or ferromagnesian (basic) rock initial materials are common parent materials for Oxisols. Indeed, it appears that one or both of these conditions is necessary for Oxisol formation (Buol et al., 1980). These authors believe that the vast majority of the Oxisols are present on highly weathered transported

material. This belief is in contrast to previous concepts of Oxisols as residual soils. Oxisols also form in rapidly weathered materials (van Wambeke et al., 1983). An example of this exception to the rule is Oxisols formed in saprolite from very mafic rocks rich in easily weatherable iron-containing minerals (Buol et al., 1980).

In many regions, Oxisols are found on old fluvial terraces, pediments, or high lying old erosion surfaces with sideslopes occupied by Ultisols, Alfisols, or even Mollisols, if mafic rock is exposed to soil formation (Buol et al., 1980). Inceptisols may be present on backslopes with associated Entisols on floodplains or steep rapidly eroding areas. On the other hand, Oxisols were found on young alluvial floodplains in Sierra Leone. There had been preweathering of the material in this case (Odell et al., 1974, cited in Buol et al).

A different pattern of geographic association occurs on the Schofield Plateau on the island of Oahu. Here, Ultisols occupy the higher geomorphic surfaces on the slopes of the Koolau Range, while Oxisols occupy the lower surfaces of the plateau down to about 30 meters above sea level (Gavenda, 1989). In his work, Gavenda suggests that, during the mapping of the island, Ultisols were mapped where a lithologic discontinuity was apparent. If this discontinuity was not readily apparent or only weakly expressed, the area was mapped as an Oxisol. He further

suggests that the discontinuity is an old erosion surface and that soils above this buried surface are derived from volcanic ash material (Gavenda, 1989).

Globally, distribution of Oxisols tends to be independent of present rainfall patterns (van Wambeke et al., 1983). This relationship is especially true of great groups which were differentiated on the basis of apparent highest degree of weathering or strength of plinthite development and expression. These two observations suggest that Oxisols derived from transported sediments attained their weathered mineralogical characteristics by processes not related to their present location (Buol et al., 1980). Preworking of the material appears possible in a long sequence of soil profiles dating to the earliest geologic eras on the Precambrian shield of central Brazil (Buol et al., 1980).

Geographically, Oxisols occur primarily in the tropics, where "there is small seasonal variation in soil temperature (and) no seasonal soil freezing ...," (van Wambeke et al., 1983). The majority of these soils are found in iso- temperature regimes (Buol et al., 1980).

Both past and present moisture regimes influence formation and continued development of the soil (van Wambeke et al., 1983). The strong leaching conditions of a humid climate favor formation and residual concentration of kaolinite and sesquioxides (van Wambeke et al., 1983).

Udic and perudic moisture regimes are considered optimal for formation of well-drained Oxisols. Although such soils may occur under aridic conditions, they are often considered to be relicts of past climatic conditions.

Ruhe's work (1964, 1965) established that climatic fluctuations affected soil genesis and distribution in Hawaii. Specific effects of climate change are difficult to distinguish. Several climatic oscillations are known to have occurred in the islands. In addition, once clay mineralogy has reached an advanced stage of weathering, it becomes increasingly difficult for subsequent climates to leave indelible imprints upon the soil. This concept has been termed "pedogenic inertia" (Bryan and Teakle, 1946, cited in Gavenda, 1989) and increases the difficulty of detection of climatic change. Finally, the superposition of profiles, which is marked by lithologic discontinuities, also poses problems. Such superposition is believed to be the rule rather than the exception in unglaciated areas (Hunt, 1972, cited in Gavenda, 1989) and is indicated by inverse or disordered weathering sequences.

There is much geologic evidence of paleoclimates in the Hawaiian Islands. This evidence includes many reports of emerged and submerged reef deposits. Reporting on a visit to Hawaii, Cady (1961) stated that "Observations from Lanai and other islands visited suggest that the

erosion history of the islands has been complex, presumably associated with Pleistocene sea level changes as well as tectonic activity." The relict shorelines of the Islands have been summarized by Stearns (1978) and the various stands of the sea range from -1,100 to +365 meters above mean sea level. In addition, stream terraces have been correlated to high stands of the sea (Macdonald et al., 1983) and changes in stream gradients on Oahu have been related to changes in the macroclimate (Ruhe, 1961 and 1965; Ruhe et al., 1965, cited in Gavenda, 1989).

Oxisols, globally, occur in a wide range of vegetational-ecological zones. The greatest areas of these soils are in tropical rainforest, scrub and thorn forest, semi-deciduous forest, and savanna vegetational zones (Buol et al., 1980). The plant tissue deposited on these soils plays an important role in providing nutrients to the ecosystem. Because of the extreme weathering, these soils have very low nutrient reserves and low exchange capacities. Thus, nearly all of the nutrients in the ecosystem are held within the living or dead plant tissue. The rapid turnover between the vegetation and the litter means that there is little involvement of the soil except for deep feeding by tree roots in lower C horizons (Buol et al., 1980).

The extreme degree of chemical decomposition seen in these soils may be a result of age as well as

weatherability of primary minerals (van Wambeke et al., 1983). Great soil age, resulting from occurrence on old land surfaces, and an associated high degree of weathering are considered to be very in the formation of Oxisols (Soil Survey Staff, 1975).

Definition of Oxisols

The following definition of Oxisols is taken from Keys to Soil Taxonomy (Soil Survey Staff, 1990). Oxisols are mineral soils that have either:

- "1. An oxic horizon with its upper boundary within 150 cm of the soil surface and do not have a clay content increase necessary to define the upper boundary of a kandic horizon within a depth of 150 cm of the soil surface, or
2. 40 percent or more clay in the surface 18 cm, after mixing, and, with its upper boundary within 150 cm of the soil surface, either an oxic horizon, or a kandic horizon that meets the weatherable mineral requirements of an oxic horizon."

The presence of this oxic horizon distinguishes Oxisols from all other soil orders. This horizon is "intended to characterize a mineral subsurface horizon of sandy loam or finer particle size with low cation exchange capacity and low weatherable mineral content," (Soil Survey Staff, 1990). Its upper boundary is at 18 cm below the soil surface, or at the base of the Ap horizon, whichever is deeper. Alternatively, its upper boundary occurs at some deeper depth where the mineralogical and

charge characteristics for the oxic horizon are met. Specifically, the oxic horizon is a subsurface horizon that:

1. Is at least 30 cm thick; and
2. Has a particle size of sandy loam or finer in the fine earth fraction; and
3. Has an apparent ECEC¹ $< 12 \text{ cmol}^{(+)} \text{ kg}^{-1} \text{ clay}$ and an apparent CEC pH 7² $< 16 \text{ cmol}^{(+)} \text{ kg}^{-1} \text{ clay}$; and
4. Does not have as much as 10 percent weatherable minerals in the 50-200 micron fraction; and
5. Has a diffuse upper particle-size boundary³; and
6. Does not have andic soil properties; and
7. Has less than 5 percent by volume that shows rock structure unless the lithorelicts containing weatherable minerals are coated with sesquioxides, (Soil Survey Staff, 1990).

Traces of weatherable minerals may be present in the oxic horizon. Three factors have been suggested to account for the occurrence of these minerals.

Sesquioxidic coatings on primary minerals, a frequent feature in soils derived from basalts, may retard their alteration. Additions of primary minerals may have

1 NH_4OAc bases plus 1N KCl-extractable Al.

2 NH_4OAc CEC.

3 i.e., less than 1.2 times clay content increase within a vertical distance of 15 cm if the surface horizon contains 20-40 percent clay; 4 percent absolute clay content increase if the surface contains 20 percent or less clay; less than 8 percent absolute if the surface contains 40 percent or more clay.

occurred during transport of the highly weathered material from which many Oxisols formed. Finally, primary minerals, deposited through aerosolic additions, may be present as contaminants. These additions are generally insignificant in terms of changing the basic characteristics of the soil, (van Wambeke et al., 1983). There is, however, evidence that such additions are not so insignificant in Hawaiian soils (Jackson et al., 1971; Swindale and Uehara, 1966; Gavenda, 1989).

The kandic horizon is intended to characterize a vertically continuous subsurface horizon of accumulation of low activity clay that is at least 30 cm thick and overlain by a coarser textured surface horizon. The charge characteristics of the clay in at least the major portion of a kandic horizon are identical to those of an oxic horizon. The requirements for clay increase are very similar to those defined for an argillic horizon.

The oxic horizon

Because Oxisols generally occur on stable surfaces, weathering has commonly proceeded to a great depth. In Hawaii, the surface layer of many Oxisols, especially those which have been cultivated, has CEC and ECEC values which exceed the definitive values for the oxic horizon. The increased CEC and ECEC are the result of additions of litter or other organic matter during cultivation.

Additions of primary minerals through deposition of tropospheric dust may also be responsible for the increase. the remaining soil depth retains the low ion exchange values and variable charge characteristics of the oxic horizon.

The field pH of some Oxisols, particularly those in Acric subgroups, is near the zero point of net charge (ZPNC) (Dixon, 1989). At this point, the anion exchange capacity (AEC) is nearly equal to the cation exchange capacity (CEC). The charge characteristics of the oxic horizon are directly related to its mineralogy. Primary minerals are transformed by weathering and leaching to kaolinite and Al- and Fe- sesquioxides (van Wambeke et al., 1983). The amount of pH-dependent charge which is developed is a function of the kind, crystallinity, and size of the minerals present in the Oxisol.

Most of the clay-sized minerals produced during weathering are poorly crystallized. Studies indicate that soil kaolinite is usually disordered and has a higher structural iron content than geological reference kaolinites (van Wambeke et al., 1983). The Fe-oxides are highly Al substituted and are finely divided but crystalline. The low crystallinity, small particle size, and high degree of substitution of these clay-sized minerals contributes to the development of a relatively

high specific surface, with its associated pH dependent positive and negative charges (van Wambeke et al., 1983).

Kaolinite, the dominant aluminosilicate clay mineral in most oxic horizons, has a low permanent charge but may develop a small but significant pH-dependent charge (van Wambeke et al., 1983). The ZPNC of kaolinite is close to pH 3, but when sesquioxides are present in large amounts, values as high as 6.3 have been measured (van Wambeke et al., 1983).

In the acid pH range, sites on the edges of kaolinite plates accept H^+ ions, thus acquiring positive charge (Dixon, 1989). Positive charge may also arise through isomorphous substitution of Al^{3+} by Ti^{4+} , although no proof of these substitutions have been reported (Dixon, 1989). The CEC of pure kaolinite measured at pH 7 was reported to be two times the value at pH 4 (Buol et al., 1980).

Coarse particles of gibbsite contribute little to the pH-dependent charge. Poorly crystallized Fe-oxides may generate significant amounts of pH-dependent charge (van Wambeke et al., 1983). In the presence of water, the Fe ions located at the surface of an oxide complete their ligand shell with hydroxyl ions and the surface becomes completely hydroxylated. This hydroxylation is then followed by the adsorption of H_2O molecules through hydrogen bonding and a monomolecular layer of water is

formed (Schwertmann and Taylor, 1989). Positive or negative charge is created at the hydroxylated or hydrated surface by adsorption or desorption of H^+ or OH^- , thus creating a surface potential.

The pH of the ZPNC of Fe oxides ranges between 7 and 9 without any marked difference between the various mineral forms. Adsorbed anions lower the ZPNC, while cations raise the ZPNC. For example, ZPNC values of 5.3 to 7.5 were found in natural ferrihydrites because of silicate adsorption (Schwertmann and Taylor, 1989).

Permanent charge arising from isomorphous substitution, which often occurs in layer silicates, contributes little or nothing to the charge of the Fe-oxides. An exception is the substitution of Ti^{4+} for Fe^{3+} , which creates positive permanent charge (Schwertmann and Taylor, 1989).

Under continuous leaching, the pH of the oxic horizon tends to shift to the pH of ZPNC of the soil material (van Wambeke et al., 1983). When the pH of the ZPNC of the soil is extremely low, the strong acidity will cause decomposition of the clay minerals and the soil pH may be buffered by Al cations at pH values near 4.5 (van Wambeke et al., 1983). Alternatively, when the ZPNC is higher, as when the active surfaces of the clay fraction are due mainly to oxides rather than organic matter and silicate minerals, soil acidity may equilibrate at the ZPNC (van

Wambeke et al., 1983). At this stage, the amount of exchangeable cations will be negligible and the phosphorus fixation potential will be high (van Wambeke et al., 1983).

The base saturation of most oxic horizons is low, and Al ions may occupy a substantial number of the available exchange sites (van Wambeke et al., 1983). Some oxic horizons have high base saturations, but it is assumed that the cations were supplied to the exchange complex subsequent to the weathering process (van Wambeke et al., 1983). Additionally, higher base saturation values are often found in oxic horizons with ustic moisture regimes, as opposed to those occurring in more humid environments (van Wambeke et al., 1983).

An extremely wide range of textures is allowed in the definition of the oxic horizon. In Hawaii, apparent field textures range from silt loam to silty clay loam to silty clay. The actual particle-size distribution (by particle size distribution analysis), however, often shows 90 to 100 percent clay. This discrepancy has been attributed to the aggregating effect of Fe-oxides (Schwertmann and Taylor, 1989). Although somewhat controversial, this effect is generally accepted. The actual mechanism of aggregation seems to vary with different soils (Schwertmann and Taylor, 1989).

Aggregation has been defined as the association of particles of the soil matrix, particularly the clay fraction, into small aggregates by minute particles of Fe-oxides (Schwertmann and Taylor, 1989). This association may form through an attraction between positively charged Fe-oxide particles and negatively charged matrix particles. The aggregation effect is probably pH-dependent, since the charge of Fe-oxide particles is also pH-dependent (Schwertmann and Taylor, 1989). In kaolinitic soils, however, transmission electron microscopy has revealed that the silty texture is due to the aggregation of Fe-oxide crystals among themselves, rather than bonding of Fe-oxide crystals to kaolinite flakes (Jones et al., 1982, cited in Schwertmann and Taylor, 1989).

Many Oxisols show low silt contents and this is related to the increased susceptibility to weathering of primary minerals when their particle size is reduced (De Alwis and Pluth, 1976, cited in van Wambeke et al., 1983). The silt fraction is dominantly quartz but it may include ilmenite and magnetite and gibbsite crystals (van Wambeke et al., 1983). Although concentrated in the clay fraction, kaolinite often occurs as fine silt (5 to 2 micrometer) and sometimes even as medium silt (20 to 5 micrometer) particles (Allen and Hajek, 1989).

The water-dispersable clay content of oxic horizons is usually negligible, and minimum values are reached at the depth where the pH of the soil approaches the ZPNC (Uehara and Keng, 1975, cited in van Wambeke et al., 1983).

The bulk density of the oxic horizon is usually low, approximately 1 to 1.3 g cm⁻³. The variation in bulk density has been attributed to variations in the sand content (van Wambeke et al., 1983).

The moisture retention characteristics of the oxic horizon are unique. Infiltration is usually rapid. Even clayey Oxisols behave like sandy soils with respect to pF curves because they rapidly lose most of the water they contain at tensions of less than 100 kPa (1 bar) (Buol et al., 1980; van Wambeke et al., 1983). At higher tensions, however, a well-aggregated, clayey Oxisol holds more water than a sand but less than a soil containing a similar amount of layer silicate clay (Sanchez, 1976). Because of these water retention characteristics, Oxisols have a narrower available water range than other clayey soils (Sanchez, 1976; van Wambeke et al., 1983). For example, if there is more than 25% clay, retention at tensions of 33kPa to 1500 kPa is roughly equal to 10 mm per 10 cm soil (van Wambeke et al., 1983).

After crushing, the structural units of the oxic horizon exhibit very fine (less than 2 mm) porous crumb

structure. The aggregates do not have well-defined shapes (van Wambeke et al., 1983) and these primary aggregates do not build up aggregates of different shapes. In old parent materials which are thoroughly weathered, the most common structure of typical oxic horizons appears to be massive but separates into very fine crumbs. By contrast, oxic horizons formed in younger parent material with clay-like textures present surfaces of weakness. These surfaces separate polyhedral peds whose faces mold to the adjoining aggregates. Aggregates of this type are usually double structured, with both large and small aggregates having the same shape (van Wambeke et al., 1983).

The stability of the aggregates in the oxic horizon is related to the aggregating effect of Fe-oxides discussed above. Iron oxide-humus complexes also contribute to aggregate stability. Studies have shown that the early hydrolysis products of hydroxypolymeric Al and Fe cations may form an effective stable bond when produced in contact with clay particles, while discrete and better crystallized Al- and Fe- oxides make poor cementing agents (El Swaify and Emerson, 1975; Greenland, 1975, cited in van Wambeke et al., 1983).

The Andisol-Oxisol Transition

In addition to similar landscape and climatic conditions, Andisols and Oxisols have some common mineralogical and chemical properties. In both orders, weathering of parent material can lead to accumulation of short-range-order minerals. In Andisols, however, the minerals are essentially aluminosilicate in composition, while oxyhydroxides of aluminum or ferric iron minerals and low activity clays dominate the mineral fraction of Oxisols. These minerals may contribute to net positive charge on soil colloids, particularly in the case of Oxisols with low organic matter levels. Andisols may also develop a net positive charge due to short-range-order aluminosilicate colloids. An analysis of the characteristics of 76 Oxisols and 41 Andepts in the Soil Management Support Services database (Kimble and Eswaran, 1988) provides some insight into the mineralogical relationship between the two orders. The distribution and magnitude of acid-oxalate-extractable Si values clearly indicate that, in contrast to Andisols, Oxisols have very low levels of allophane.

The levels of $\text{Al}_2\text{O}_3 + 1/2 \text{Fe}_2\text{O}_3$ which are found in Andisols may also be found in Oxisols which have undergone extreme weathering. The $\text{Al}_2\text{O}_3 + 1/2 \text{Fe}_2\text{O}_3$ of the Los Ulmos soil from Chile is 1.7%. This value approaches the levels

required for Andisols. In fact, when only bulk density and P retention are considered, the pedon is andic. Because the soil fails to meet the $Al_0 + 1/2 Fe_0$ requirement, it is classified as an Andic Hapludox (Kimble and Eswaran, 1988).

The relationship between $Al_0 + 1/2 Fe_0$ and CEC (NH_4OAc at pH 7.0) was also appraised in the database analysis. As expected, the Oxisols show low levels of both $Al_0 + 1/2 Fe_0$ and CEC, although there is a small overlap between soils of both orders (Kimble and Eswaran, 1988).

Andisols, by definition, must have a bulk density which is less than 0.9 g cm^{-3} . Except in the case of humus-rich soils, Oxisols do not have such low bulk densities. Typical bulk densities range from 1.1 to 1.2 g cm^{-3} .

In their review of the Andisol-Oxisol transition, Kimble and Eswaran (1988) question whether the low bulk densities exhibited by Andisols are truly a result of the mineral constituents or a reflection of accumulated organic matter. To answer this question, they analyzed several pedons of "transitional" soils.

One of these soils, a pedon from Western Samoa, had been classified as an Andic Haploperox, yet possessed nearly all the definitive characteristics of an Andisol. The bulk density of the 33 to 50 cm layer, however, was

0.91 g cm⁻³, and the soil was not classified as an Andisol. Kimble and Eswaran, therefore, suggested that this soil would be more appropriately considered as an Oxic subgroup of an Andisol, rather than an Oxisol.

Kimble and Eswaran also analyzed the influence of organic C on bulk density. Although the correlation between bulk density and organic C was low for both Andisols and Oxisols ($r^2 = 0.39$ and 0.19 , respectively), the trend of a scatter plot of the data indicates that bulk density decreases as the organic C increases.

Other common properties are phosphate retention and 1500 kPa water. The database analysis reveals a group of Oxisols with phosphate retention values greater than the critical limit of 85% (Kimble and Eswaran, 1988). This relationship demonstrates that phosphate retention is a property shared by both orders and should not be used as a class criterion by itself.

Neither order demonstrated a clear distribution pattern for 1500 kPa water. The authors, therefore, suggest that there is no need to use this value for estimation of clay content in Andisols, since the colloid fraction is in the form of a gel (Kimble and Eswaran, 1988). Clay estimation using 1500 kPa water is necessary in Oxisols, however, because of the problems with clay dispersion (Kimble and Eswaran, 1988).

Although these orders have convergent properties, the most recent revision of Soil Taxonomy has provided logical places for soils of both orders (Kimble and Eswaran, 1988). Andic subgroups of Oxisols express the subordinate properties of low bulk density and high phosphorus retention. Vitrandic subgroups recognize Oxisols which contain more than 60% of volcaniclastic materials. These subgroups are known to occur in the Haploperox, Kandiperox, Hapludox, and Kandiudox great groups. Andisols with an oxic horizon within 125 cm of the surface are classified as Oxic subgroups of the Hapludand and Haplustand great groups.

There is a need to further understand the properties of those soils with both andic and oxic characteristics in order to manage them more efficiently for agricultural purposes. In light of the recent revisions in the soil orders of Andisols and Oxisols, there is also a need to examine the taxonomic classification of these soils with andic and oxic properties.

CHAPTER 3

MATERIALS AND METHODS

The Soil Series

Published and unpublished data of eight pedons from six soil series were used to differentiate soils with either andic, oxic, or andic-oxic properties: Akaka, Oli, Kapaa, Molokai, Kolekole, and Mahana. The Akaka and Oli soils represent highly weathered Andisols, while the Kapaa and Molokai soils represent highly weathered and moderately weathered Oxisols, respectively. The Kolekole and Mahana soils, on the other hand, are thought to represent soils with andic-oxic properties. The taxonomic classification of these soils is listed in Table 3.1, while their narrative descriptions are available in Appendix 1.

Table 3.1 Taxonomic classification of the soils.

<u>Soil series</u>	<u>Classification prior to revision</u>
Akaka	Typic Hydrandepts, thixotropic, isomesic
Oli	Oxic Dystrandepts, medial, isothermic
Kapaa	Typic Gibbsihumox, clayey, gibbsitic, isothermic
Molokai	Typic Torrox, clayey, kaolinitic, isohyperthermic
Kolekole	Ustoxic Humitropepts, fine, oxidic, isothermic
Mahana	Typic Acrohumox, clayey, oxidic, isothermic

Source: Sato et al., 1973 and Foote et al., 1972.

The Akaka soil is derived from andesitic ash on the eastern slopes of Mauna Kea, on the island of Hawaii. The soil occurs at elevations ranging from 300 to 1370 m. Mean annual rainfall is 6600 mm. The soil is moderately well-drained and has an apparent field texture (AFT) of silty clay loam throughout the profile.

In contrast, the Oli soil on Kauai is developed from volcanic ash deposited over basic igneous rock. The soil occurs on uplands at elevations from 300 to 700 m. The annual rainfall ranges from 760 to 1020 mm. The soil is typically silt loam (AFT). Vents of the Koloa Volcanic Series may be the source of the ash from which the Oli soil is derived. According to Macdonald et al. (1983), the K-Ar age of the Koloa Volcanic Series is 1.5 million years.

In contrast to the ash-derived Akaka and Oli soils, the Kapaa soils formed in material weathered from basic igneous rock of the Koloa Volcanic Series. This soil occurs on uplands on the island of Kauai, at elevations ranging from 60 to 240 m. The annual rainfall amounts to 2030 to 3050 mm.

The Molokai soil developed in material weathered from basic igneous rock. The soil occurs on uplands at elevations ranging from nearly sea level to 300 m. The average annual rainfall is 570 mm (Foote et al., 1972). The soil is well-drained and is silty clay loam (AFT). On

the Schofield Plateau on the island of Oahu, the parent material has been identified as basaltic rocks of the Koolau Volcanic Series, erupted during the Tertiary period (Macdonald et al., 1983).

According to the published soil survey (Foote et al., 1972), the Kolekole soil is derived from old gravelly alluvium mixed with volcanic ash. The soil occurs on uplands bordering the windward side of the Waianae Range on the island of Oahu, at elevations ranging from 150 to 370 m. The annual rainfall ranges from 890 to 1270 mm. The soil is well-drained, with a silty clay loam surface (AFT). The parent material is likely to be the Kolekole Volcanics lithologic unit. This unit is mid-Pleistocene in age (Macdonald et al., 1983).

The Mahana soil developed in volcanic ash on uplands on the islands of Kauai and Oahu at elevations ranging from 300 to 900 m (Foote et al., 1972). The annual rainfall ranges from 760 to 1150 mm. In a representative profile, the surface layer is silt loam (AFT). The subsurface is silt loam to silty clay loam (AFT). On Kauai, ash of the Koloa Volcanic Series is the likely parent material, while on Oahu, ash of the Kolekole Volcanics is the likely parent material of the respective Mahana soils. Both of these lithologic units erupted during the Pleistocene period.

Three soils were collected on the island of Oahu for this study. One of the Mahana soils was sampled near Puu Makakilo ($21^{\circ} 22' 37''$ N latitude, $158^{\circ} 05' 37''$ W longitude). This soil will be referred to as "Mahana (Oahu)". The Kolekole soil (Kolekole I) was sampled from a roadbank near the Hawaii Country Club on Kunia Road ($21^{\circ} 27' 04''$ N latitude, $158^{\circ} 03' 46''$ W longitude), while the Molokai soil was sampled from a roadbank in a field belonging to the Oahu Sugar Company. This site was located on Kunia Road, approximately 2.72 km north of the intersection of Farrington Highway and Kunia Road ($21^{\circ} 24' 27''$ N latitude, $158^{\circ} 02' 49''$ W longitude).

The Oli soil and another Mahana soil were collected on the island of Kauai previously. Information relating to the Akaka soil from the island of Hawaii and the Kapaa soil from Kauai was obtained from Soil Survey Investigation Report 29 (SSIR 29) (Soil Conservation Service, 1976). Information relating to a second sample of the Kolekole soil (Kolekole II) was taken from the unpublished dissertation of R. Gavenda (1989).

The Laboratory Data

The soil samples were air-dried and ground to pass a 2-mm sieve. Bulk density was determined by the paraffin-coated method as described in SSIR 1 (Soil Conservation Service, 1972). Soil pH was measured in both water and 1N

KCl solution (1:1 volume ratio of soil to water or KCl solution) and after allowing the soil suspension to stand overnight (Soil Conservation Service, 1972).

Unpublished data of H. Ikawa, A. Chu, and R. Gavenda were also used in this study. They include moisture retention data at 1500 and 33kPa as determined by the pressure plate method; cation exchange capacity and the exchangeable bases by the ammonium acetate pH 7 extraction; and KCl-extractable Al. All of these items were collected according to methods described in SSIR 1 (Soil Conservation Service, 1972).

In addition, acid-oxalate-extractable Al and Fe and phosphate retention were determined according to the New Zealand method of Blakemore et al. (1987). Other published data regarding organic C and mineralogy were also consulted.

The m Value

The m value in this study was developed to reflect the magnitude of the variable charge carried by the soil system. It was derived by plotting the cation exchange status of the soil against the pH at which the status was measured (field pH (1:1 H₂O) and pH 7). The variable charge indicator m, therefore, is equal to the slope of the line which connects the point which represents the CEC (NH₄OAc) determined at pH 7 with the point which represents the ECEC determined at field pH.

The m value is expressed as follows:

$$m = (y_2 - y_1) / (x_2 - x_1)$$

where $(x_2, y_2) = (\text{pH } 7, \text{ CEC})$ and

$(x_1, y_1) = (\text{field pH, ECEC})$.

The term m is the variable charge indicator for the whole soil. The term m' has also been provided and is the variable charge indicator for the calculated clay fraction expressed as $\text{cmol}(+) \text{ kg}^{-1}$ clay. In the case of andic materials, it should be noted that because the colloidal fraction acts more as a gel than a crystalline clay system, calculating an estimated clay percentage may be inappropriate. The calculation, however, has been included for these materials in order to investigate its usefulness.

The Taxonomic Classification of Soils

Published and unpublished data, as well as soil descriptions, were used to classify the soils according to the latest revisions in Soil Taxonomy (Soil Survey Staff, 1990). The classification is provided for the pedons only because these soils are not necessarily representative of the official series concept.

CHAPTER 4

RESULTS AND DISCUSSION OF RESULTS

The Soils and Their Properties

Table 4.1 shows the laboratory data used to classify the Akaka soil as an Andisol. The main requirements of Andisols are the acid-oxalate-extractable Al and Fe, low bulk density, and high phosphate retention. The phosphate retention data is unavailable here, but other studies have shown that the phosphate retention of the Akaka soil is great enough to meet requirements for the Andisol order. Other secondary characteristics supporting the presence of andic properties include high water retention at 33 kPa, and high available water capacity. Available water capacity is defined as the difference in water retention between 33 and 1500 kPa. A high CEC indicates high chemical activity and also supports the presence of andic properties.

Based on the data in Table 4.1, the Kapaa soil is classified as an Oxisol. The main requirements for this order are low CEC and ECEC and the lack of primary minerals. The CEC and ECEC data is incomplete because the calculated clay percentage (3×1500 kPa) was greater than 100% in 3 horizons. Other research, however, has shown that the Kapaa soil meets the requirements for the Oxisol order (SCS, unpublished data). The high degree of

Table 4.1 Selected chemical and physical data of Akaka and Kapaa soils.

Soil	Horizon	Depth (cm)	CEC -cmol(+)/kg clay-	ECEC	m ¹	Al ₂ O ₃ + 1/2Fe ₂ O ₃ (%)	PO ₄ Ret. %	B.D. (g/cm ³)	Water Retention 1500 kPa wt. %	Available 33 kPa wt. %	Water Cap Water Cap wt. %	pH H ₂ O	pH KCl	Delta pH
Akaka	Ap1	0-25	170.8	13.6	71.4	7.5	nd	nd	31.9	48.1	16.2	4.8	nd	nd
	Ap2	25-43	257.7	6.9	139.4	9.8	nd	nd	27.9	37.1	9.2	5.2	nd	nd
	Bw1	43-71	96.5	2.2	49.6	5.4	nd	nd	25.2	135.3	110.1	5.1	nd	nd
	Bw2	71-96	137.6	2.2	67.7	9.3	nd	nd	24.1	173.7	149.6	5.0	nd	nd
	Bw3	96-104	131.8	2.1	64.9	9.9	nd	nd	26.6	313.2	286.6	5.0	nd	nd
	Bw4	104-112	293.8	2.8	153.1	8.3	nd	nd	33.2	nd	nd	5.1	nd	nd
	Bw5	112-120	268.8	2.6	140.1	10.5	nd	nd	32.5	201.4	168.9	5.1	nd	nd
	BC	120-152	330.4	2.9	172.3	9.1	nd	nd	7.4	179.8	172.4	5.1	nd	nd
Kapaa	Ap	0-35	19.5	2.1	7.9	nd	nd	1.3	28.4	34.7	6.30	4.8	4.4	-0.4
	B21	35-55	nd	nd	nd	nd	nd	nd	34.1	39.6	5.50	5.8	6.1	0.3
	B22	55-78	1.90	0.42	2.12	nd	nd	1.2	31.5	37.7	6.20	6.3	6.3	0.0
	B23	78-95	nd	nd	nd	nd	nd	nd	35.1	42.6	7.50	5.8	6.1	0.3
	B24	95-113	nd	nd	nd	nd	nd	nd	38.1	43.0	4.90	5.8	5.8	0.0
	B25	113-150	2.09	0.44	1.18	nd	nd	1.19	30.3	37.4	7.10	5.6	5.7	0.1

nd: no data available

Source: Soil Survey Investigations Report #29, Soil Conservation Service, 1972.

weathering in this soil is indicated by the positive delta pH values in the B horizons.

Table 4.2 shows the results of the analysis of the Oli and Mahana soils from Kauai. As shown in Table 3.1, the Oli soil series is classified as a medial, isothermic Oxic Dystrandept, whereas the Mahana soil series is classified as a clayey, oxidic, isothermic Typic Acrohumox.

All of the data that are necessary to classify these soils according to the latest revision of Soil Taxonomy were not available at the time of this writing. The data in Table 4.2, however, reveal that the Oli soil meets neither the phosphate retention requirement of the Andisol order nor the CEC and ECEC requirements of the Oxisol order. Only the Bw3 horizon of the Mahana (Kauai) soil meets the definition of andic properties. At the same time, the high CEC values in the other horizons do not meet the requirements of the oxic horizon.

Table 4.3 lists the chemical and physical properties of the Kolekole, Mahana, and Molokai soils from Oahu. As explained previously, the data of Kolekole I are from Ikawa and Chu (unpublished data) while those of Kolekole II are from Gavenda (1989). Again, certain data elements were unavailable at the time of this writing, but the available data show that only certain horizons of the Kolekole soil meet the requirements of

Table 4.2 Selected chemical and physical data of Oli and Mahana soils from Kauai.

Soil	Horizon	Depth	CEC *	ECEC *	m'	Al ₂ O ₃ + 1/2Fe ₂ O ₃ #	PO ₄ Ret. #	B.D.*	Water Retention*		Avail.	pH	pH	Delta
		(cm)	-cmol(+)/kg clay-			%	%	(g/cm ³)	1500 kPa wt. %	33 kPa wt. %	H ₂ O Cap.* wt. %	H ₂ O *	KCl *	pH *
Oli	A	0-26	35.4	5.9	10.2	nd	68	nd	19.1	30.4	11.3	4.1	4.0	-0.1
	Bw1	26-50	26.1	2.0	13.4	nd	87	nd	26.0	37.8	11.8	5.2	4.3	-0.9
	Bw2	50-75	23.4	4.9	8.4	nd	77	nd	25.7	32.3	6.7	4.8	3.9	-0.9
	Bw3	75-90	23.9	5.4	8.8	nd	78	nd	25.2	33.8	8.6	4.9	3.9	-1.0
Mahana	A1	0-6	27.5	4.6	9.6	nd	47	1.22	22.6	41.7	19.1	4.6	3.8	-0.8
	A2	6-20	23.5	6.3	6.6	nd	59	0.82	23.0	48.5	25.5	4.4	3.9	-0.5
	Bw1	20-43	27.9	2.5	11.1	nd	87	0.73	28.7	58.3	29.6	4.7	4.2	-0.5
	Bw2	43-69	nd	nd	nd	nd	98	0.70	54.6	65.6	11.0	4.7	4.4	-0.3
	Bw3	69+	nd	nd	nd	nd	nd	0.98	nd	49.8	nd	nd	nd	nd

nd: no data available

* Source: H. Ikawa (unpublished data)

Source: A. Chu (unpublished data)

Table 4.3 Selected chemical and physical data of Kolekole, Mahana, and Molokai soils from Oahu.

Soil	Horizon	Depth (cm)	CEC * -cmol(+)/kg clay-	ECEC *	m'	Alo + 1/2Feo # %	PO4 Ret.# %	B.D.* (g/cm3)	Water Retention* 1500 kPa wt.%	33 kPa wt.%	Avail. H2O Cap.* wt.%	pH H2O *	pH KCl *	Delta pH *
Kolekole I	Ap1	0-15	40.9	9.8	13.5	nd	78	nd	19.7	31.0	11.3	4.7	4.2	-0.5
	Ap2	15-41	31.7	11.4	10.7	nd	69	0.95	19.6	30.2	10.7	5.1	4.4	-0.7
	Bw1	41-58	36.1	12.1	13.3	nd	77	1.03	21.9	33.9	12.0	5.2	4.4	-0.8
	Bw2	58-86	21.2	10.9	4.7	nd	57	1.33	27.7	34.3	6.6	4.8	4.1	-0.7
	Bw3	86-100	22.4	7.7	5.9	nd	69	1.21	30.9	38.8	7.9	4.5	4.0	-0.5
	2Bw1	100-116	26.3	6.3	8.3	nd	88	0.94	31.9	42.7	10.7	4.6	4.1	-0.5
	2Bw2	116-141	nd	nd	nd	nd	96	0.85	37.5	58.7	21.2	4.6	4.4	-0.2
	3Bc	141-175	24.5	15.4	2.9	nd	47	1.67	22.4	26.5	4.0	3.9	3.7	-0.2
Kolekole II a	A1	0-25	24.1	8.4	4.8	nd	nd	1.33	22.3	nd	nd	3.7	nd	nd
	A2	25-60	26.9	8.2	5.5	nd	83	1.04	22.8	nd	nd	3.6	nd	nd
	2Bw1	60-85	82.5	3.3	31.7	2.62	99	0.65	56.5	nd	nd	4.5	nd	nd
	2Bw2	85-100	82.4	2.4	33.4	nd	nd	0.82	52.5	nd	nd	4.6	nd	nd
	2Bw3	100-118	95.6	2.9	37.1	5.89	99	0.66	66.9	nd	nd	4.5	nd	nd
	3Bct1	118-138	32.9	4.7	9.7	nd	82	1.57	23.2	nd	nd	4.1	nd	nd
	3Bct2	138-160	23.7	8.4	4.8	nd	nd	1.62	27.0	nd	nd	3.8	nd	nd
	3Bct3	160-190	21.2	7.2	4.5	nd	nd	1.60	27.2	nd	nd	3.9	nd	nd
Mahana	A1	0-8	46.6	24.6	11.5	nd	40	1.02	20.7	36.5	15.8	5.1	4.4	-0.7
	A2	8-21	40.0	14.2	13.6	nd	49	1.16	21.0	34.4	13.4	5.1	4.0	-1.1
	Bw1	21-34	30.8	12.1	9.3	nd	55	1.10	27.2	39.7	12.5	5.0	3.8	-1.2
	Bw2	34-58	33.1	10.7	10.2	nd	66	1.13	28.3	43.7	15.3	4.8	3.7	-1.1
	Bw3	58-84	31.1	11.6	8.1	nd	67	1.39	27.9	34.4	6.5	4.6	3.6	-1.0
Molokai	Ap1	0-14	33.0	29.0	4.9	nd	35	nd	19.8	30.5	10.8	6.2	5.6	-0.6
	Ap2	14-38	31.2	27.3	6.5	nd	34	nd	20.2	29.4	9.1	6.4	5.6	-0.8
	Bo1	38-57	17.9	13.0	8.1	nd	40	nd	19.5	29.5	9.9	6.4	5.8	-0.6
	Bo2	57-75	15.2	12.3	4.7	nd	39	nd	19.8	28.1	8.3	6.4	5.9	-0.5
	Bo3	75-96	15.4	10.7	7.9	nd	41	nd	21.7	28.4	6.6	6.4	6.1	-0.3
	Bo4	96-117	14.9	11.0	5.5	nd	44	nd	22.2	29.2	7.0	6.3	6.1	-0.2
	Bo5	117-129	14.4	11.9	2.7	nd	45	nd	22.2	28.7	6.5	6.1	6.0	-0.1
	Bo6	129-160	14.9	14.3	0.8	nd	52	nd	22.5	29.3	6.8	6.2	5.9	-0.3

a Source: R. Gavenda (unpublished data)

* Source: H. Ikawa (unpublished data)

Source: A. Chu (unpublished data)

andic properties. The Mahana (Oahu) soil is not an Andisol because of the low phosphate retention and high bulk density in all horizons. This soil does not classify as an Oxisol because of the high CEC throughout the profile. In contrast, the lower horizons of the Molokai soil constitute an oxic horizon, thereby allowing this soil to be as an Oxisol.

Although Tables 4.2 and 4.3 reveal that the Kolekole soils and the Mahana soils (both Oahu and Kauai) as well as the Oli soil may not be classified as Andisols or Oxisols, selected horizons of these soils suggest the influence of volcanic ash and hence, the properties of Andisols. These horizons include two horizons (2Bw1 and 2Bw2) of the Kolekole I soil, two horizons (Bw1 and Bw2) of the Mahana (Kauai) soil, and one horizon (Bw1) of the Oli soil. Furthermore, four horizons of these soils have bulk density values which are low enough to meet the criteria for andic soil properties. Only two horizons, Kolekole I (2Bw2) and Mahana (Kauai) (Bw2), however, possess both of these characteristic properties. The latter horizon also has acid-oxalate-extractable Al plus one-half acid-oxalate-extractable Fe ($Al_0 + 1/2 Fe_0$) which is > 2 percent. No data were available for the Kolekole I horizon. If $Al_0 + 1/2 Fe_0$ is assumed to be > 2.0 percent in the Kolekole I horizon, then both of these horizons meet the requirements of andic soil properties. In

addition, both the Kolekole I and Mahana horizons have high water retention values at both 1500 and 33 kPa moisture tensions. The chemical and physical properties of these horizons, therefore, provide strong evidence of volcanic ash influence.

Several additional observations suggest that the remaining soil horizons also have been influenced by or derived from volcanic ash. For example, the published soil surveys of Hawaii describe volcanic ash as being either the parent material or the influential factor in the development of the Kolekole, Mahana, and Oli soil series. The geological record provides evidence of thin ash falls on Oahu and Kauai as well as several potential sources of volcanic ash parent material on both islands (Appendix 1). In addition, field observations made by Gavenda (1989) and during this investigation suggest that the Kolekole and Mahana soils retain the morphology of ash-derived soil. The soils in this study, however, have bulk density values which are too high in some horizons with phosphate retention values which are too low to meet the requirements of andic soil properties. These soils may meet the andic soil requirements if they meet the second set of requirements (vis a vis glass versus $Al_2O_3 + 1/2Fe_2O_3$) which have not been determined in this study. Although the CEC values shown in Tables 4.2 and 4.3 are not low enough, the ECEC values for nearly all of the

horizons are low enough to meet the requirements for the oxic horizon.

The data presented in this study so far suggests that there is a transition in the weathering continuum between Andisols and Oxisols. The question of the position of these soils in the continuum in relation to each other will be answered by examining the variable charge indicator m . This indicator is described in Chapter 3, Materials and Methods.

The m Values and Andic-Oxic Soils

Table 4.4 shows the calculated variable charge indicator m for the soils examined in this study. The m values for the Akaka and Kapaa soils illustrate some important relationships. A variation in m from 2.4 in the Kapaa B₀₁ horizon to 18.3 in the Akaka B_{w2} horizon is much more expressive of the difference in variable charge between the two systems than is the change in m from the B_{w1} to the B_{w2} horizon of the Akaka soil.

Small variations in m become more important as m decreases, especially when evaluated in conjunction with bulk density and phosphate retention. The effect of changes in the environmental pH on Fe-oxides may be responsible for these variations. As the ZPNC of the system approaches the natural pH value of the soil, the polarity of the net charge becomes more susceptible to

Table 4.4. The m and m' values of soils with andic-oxic properties.

Soil	Horizon	Depth (cm)	CEC * ----- meq/100g -----	ECEC *	m	m'
Akaka	Ap1	0 - 25	52.6	4.2	22.0	71.4
	Ap2	25 - 43	45.1	1.2	24.4	139.4
	Bw1	43 - 71	30.1	0.7	15.5	49.6
	Bw2	71 - 96	37.3	0.6	18.3	67.7
	Bw3	96 - 104	51.4	0.8	25.3	64.9
	Bw4	104 - 112	51.7	0.5	26.9	153.1
	Bw5	112 - 120	51.6	0.5	26.9	140.1
	BC	120 - 152	33.7	0.3	17.6	172.3
Kapaa	Ap	0 - 35	16.6	1.8	6.7	7.9
	Bo1	35 - 55	3.4	0.5	2.4	na
	Bo2	55 - 78	1.8	0.4	2.0	2.1
	Bo3	78 - 95	4.2	0.7	2.9	na
	Bo4	95 - 113	4.3	1.1	2.7	na
	Bo5	113 - 150	1.9	0.4	1.1	1.2
Oli	A	0 - 26	20.30	3.39	5.8	10.2
	Bw1	26 - 50	20.34	1.57	10.4	13.4
	Bw2	50 - 75	18.04	3.81	6.5	8.4
	Bw3	75 - 90	18.06	4.06	6.7	8.8
Mahana (Kauai)	A1	0 - 6	18.67	3.11	6.5	9.6
	A2	6 - 20	16.17	4.33	4.6	6.6
	Bw1	20 - 43	24.02	2.12	9.5	11.1
	Bw2	43 - 69	46.77	2.12	19.4	nd
	Bw3	69+	nd	nd	nd	nd
Kolekole I	Ap1	0 - 15	24.24	5.81	8.0	13.5
	Ap2	15 - 41	18.60	6.70	6.3	10.7
	2Bw1	41 - 58	23.70	7.96	8.7	13.3
	2Bw2	58 - 86	17.62	9.05	3.9	4.7
	2Bw3	86 - 100	20.82	7.19	5.5	5.9
	3Bct1	100 - 116	25.15	6.05	8.0	8.3
	3Bct2	116 - 141	35.34	3.75	13.2	na
	3Bct3	141 - 175	16.46	10.36	2.0	2.9
Kolekole II @	A1	0 - 25	24.10	8.41	4.8	4.8
	A2	25 - 60	26.90	8.15	5.5	5.5
	2Bw1	60 - 85	82.50	3.25	31.7	31.7
	2Bw2	85 - 100	82.40	2.36	33.4	33.4
	2Bw3	100 - 118	95.60	2.86	37.1	37.1
	3Bct1	118 - 138	32.90	4.71	9.7	9.7
	3Bct2	138 - 160	23.70	8.36	4.8	4.8
	3Bct3	160 - 190	21.20	7.16	4.5	4.5
Mahana (Oahu)	A1	0 - 8	28.89	15.29	7.2	11.5
	A2	8 - 21	25.16	8.94	8.5	13.6
	Bw1	21 - 34	25.15	9.88	7.6	9.3
	Bw2	34 - 58	28.14	9.06	8.7	10.2
	Bw3	58 - 84	26.04	9.68	6.8	8.1
Molokai	Ap1	0 - 14	19.56	17.22	2.9	4.9
	Ap2	14 - 38	18.95	16.6	3.9	6.5
	Bo1	38 - 57	10.46	7.60	4.8	8.1
	Bo2	57 - 75	9.02	7.33	2.8	4.7
	Bo3	75 - 96	10.02	6.94	5.1	7.9
	Bo4	96 - 117	9.90	7.34	3.7	5.5
	Bo5	117 - 129	9.56	7.92	1.8	2.7
	Bo6	129 - 160	10.06	9.63	0.5	0.8

nd: no data available

* Source: H. Ikawa (unpublished data)

@ Source: R. Gavenda (unpublished data)

small changes in environmental pH (Schwertmann and Taylor, 1989).

Soils dominated by "amorphous materials" (minerals of short range order) would be expected to show great differences between CEC and ECEC values and hence to show high m values (steep slopes). In contrast, soils dominated by crystalline minerals would be expected to have less variable charge, as indicated by low m values and flatter slopes. The mineralogy of both the Akaka and Kapaa series, combined with the results of the chemical analysis conducted in this study, support this conclusion.

Research conducted by Wada and Wada (1976) reveals that the B horizons of the Akaka soil were characterized by the predominance of hydrous noncrystalline alumina and iron oxides. These oxides were associated with considerable amounts of humus and with very small amounts of silica. Allophanic materials (allophane, allophane-like constituents, and imogolite) were present in minor amounts. Gibbsite, goethite, chlorite, and illite were present only as accessory minerals, with gibbsite as the main constituent of both the sand and silt fraction. The dominance of hydrous noncrystalline materials in this soil suggests high variable charge characteristics, and the data reported in Table 4.1 confirm this conclusion. The variable charge indicator m ranges from 15.5 to 26.9, while the variable charge indicator m' ranges from 49.6 to

172.3. For soils such as the Akaka which are dominated by gel colloidal systems, calculating clay-based m' values may be inappropriate.

In contrast to the Akaka soil, the Kapaa soil is dominated by the crystalline minerals gibbsite, goethite, and kaolinite (SCS, 1976). Anatase, magnetite, and small amounts of mica (less than 5%) are also reported. As predicted, the m values for this soil range from 6.7 in the surface to 1.1 at depth, with m' values being only slightly different, ranging from 7.9 to 1.2 (Table 4.4).

The high m values in the surface horizons of the Kapaa soil, relative to subsurface horizons (Table 4.4), illustrate another relationship between variable charge and soil constituents. Horizons which have large amounts of organic matter should have high m values (steep slopes) which reflect the variable charge characteristics of soil organic matter.

The Akaka Ap1 horizon illustrates the influence of both "amorphous" mineralogy and organic matter accumulation. Curiously, analysis of the m values for the surface horizons of each profile studied reveals that the surface horizon does not always possess the greatest variable charge. This phenomenon may reflect changes in mineralogy and/or soil parent material with depth as well as variations in organic matter due to cultivation or rate of decomposition.

Based on the observations in this study, the variable charge indicator m may be used to establish two boundaries which isolate soils with both andic and oxic properties. All of the andic horizons identified in Tables 4.1, 4.2, and 4.3 have m values greater than 15. The only exception is the Kolekole I (2Bw2) horizon. This horizon, however, cannot be identified positively as an andic horizon without the acid-oxalate-extractable Al and Fe data.

In contrast, each of the Kapaa horizons (with the exception of the Ap horizon) and all of the Molokai horizons which meet oxic characteristics have m values which are < 5.5 . The higher m value of the Kapaa Ap horizon may be attributed to higher content of organic matter. Soils with both andic and oxic properties, or "andic-oxic" soils, therefore, may be defined as soil material which does not meet the requirements established for either the andic or oxic soil material and which have m values greater than or equal to 5.5, yet less than 15.

This definition effectively isolates soils with both andic and oxic properties in all but three cases. Both the Kolekole I Bw2 and 3BC horizons have CEC and ECEC values ($\text{cmol}(+) \text{ kg}^{-1} \text{ clay}$) which are greater than those defined for oxic materials. Both m and m' , however, are < 5.5 in both horizons. The third exception is the Mahana (Kauai) A2 horizon, which has CEC and ECEC values ($\text{cmol}(+) \text{ kg}^{-1} \text{ clay}$) which are too high to meet the requirements for

oxic material. The variable charge indicator m is < 5.5 , but m' is slightly > 5.5 .

These exceptions appear to indicate that m' would be a more appropriate boundary-defining value if adequate clay dispersion and accurate percent clay values could be assured. Examination of the calculated data, however, shows that m is more successful at isolating soils with both andic and oxic characteristics from soils with definite oxic characteristics.

The mineralogy of the "andic-oxic" soils supports the establishment of these boundaries. For example, x-ray diffractograms of the Mahana (Kauai) soil suggest the presence of amorphous materials and the absence of kaolinite. The amorphous materials are slightly more dominant in the Bw2 horizon than in the upper Bw1 horizon. This dominance is reflected in the high m value of 19.4. As discussed previously, this horizon meets all the requirements for andic soil properties. In addition, higher amounts of quartz, received through aerosolic additions of tropospheric dust (Rex et al., 1969; Jackson et al., 1971), are present in the surface horizons when compared with the subsurface horizons.

X-ray diffraction analysis of the Mahana (Oahu) profile reveals the presence of small amounts of kaolinite. Quartz is also present and decreases with depth. The m values of each horizon are very similar and

the differences are small enough that they may be attributed to experimental error or small differences in clay percent or type. The similarity between the m values may reflect the presence of small amounts of kaolinite in each horizon within a soil profile.

The mineralogy of the Kolekole soil is somewhat controversial. As reported by Wada and Wada (1976) for a soil profile collected at the same site as Kolekole I (Gavenda, 1990, personal communication), the B horizons were characterized by predominance of kaolinite, hematite, and goethite. The x-ray diffraction analysis revealed the presence of more hematite than goethite. The dithionite-citrate soluble fraction was composed of Al_2O_3 and Fe_2O_3 in roughly equal amounts, and the acid-oxalate extraction indicated a low noncrystalline iron oxide content. Kaolinite and hematite, with some goethite, were the main constituents of the silt fraction and magnetite was identified in the fine sand fraction.

The presence of imogolite and allophane, occurring as weathering products of basalt saprolite on Maui, had been reported in previous research (Patterson, 1964; Wada et al., 1972). Neither imogolite nor allophane, however, was found in the Kolekole clay (Wada and Wada, 1976). Instead, their results suggest that a considerable portion of the humus in the Kolekole soil formed complexes with Al ions, such complexes being common in volcanic ash soils.

An admixture of volcanic ash was described in the published soil survey (Foote et al., 1972), and the results reported by Wada and Wada (1976) lend support to this description.

Gavenda (1989) suggests that rather than being influenced by an admixture of ash, the B horizons of the Kolekole series developed in ash. His work also describes a complex series of erosional and depositional events by which ash was deposited in the Wahiawa Basin. X-ray diffractograms of B horizons from two Kolekole pedons indicate the presence of short-range-order minerals. X-ray diffractograms of the deeper horizons such as the 3Bct2 horizon of Kolekole II, however, reveal mineralogy which is similar to that described by Wada and Wada (1976). The m values of both Kolekole pedons reflect this variability in mineralogy. For example, the 2Bw2 and 2Bw3 horizons of the Kolekole I profile have m values less than or equal to 5.5, while the m values of the two horizons immediately beneath them are significantly higher (8.0 and 13.2, respectively). A similar situation is seen in the Kolekole II profile. The 2Bw horizons exhibit significantly greater m values than the 3Bct horizons beneath them. These data tend to support Gavenda's assertion that rather than an admixture of ash throughout the profile, the B horizons of the Kolekole series developed in volcanic ash, while the lower horizons

developed in deposits of alluvium (consisting of weathered basalt) washed from the Waianae Range.

Because Gavenda (1989) suggests that the Oxisols in the Wahiawa Basin were developed in volcanic ash rather than in weathered basalt, the Molokai soil was included in this study. Neither the mineralogy of the soil as analyzed by Wada and Wada (1976) nor the chemical and physical analyses performed in this study support Gavenda's assertion that the Molokai soil is ash influenced.

The B horizons of Wada's Molokai soil were characterized by predominance of kaolinite, hematite, and goethite (Wada and Wada, 1976). Clay contents of 70 to 80 percent were found. The dithionite-citrate soluble fraction of the clay was nearly exclusively composed of Fe_2O_3 , mainly as hematite. The Fe oxides formed crystals which were fine (40 - 80 Å) and were often clustered to form larger aggregates. The main crystalline constituent of the clay was kaolinite with minor amounts of illite. The silt fraction of the same soil consisted mainly of kaolinite and hematite. Allophane and imogolite, on the other hand, were absent. Wada and Wada (1976) ascribed the absence of these minerals in a soil formed in weathered basalt to the fairly dry climate under which the soil is formed. The m values for every horizon in the Molokai soil used in this study are less than 5.5 (Table

4.3). These values also suggest that the Molokai soil is dominated by crystalline minerals rather than allophane and imogolite. Thus, the results of this study concur with those of Wada and Wada (1976).

By definition, Andisols exhibit high phosphate retention and have low bulk density values. Most Oxisols, in contrast, have lower phosphate retention and bulk density values which range from 1.1 to 1.3 g cm⁻³, although there are exceptions (Kimble and Eswaran, 1988). In addition, Andisols must have Al₂O₃ + 1/2Fe₂O₃ levels which are greater than 2 percent. In most cases, the Al₂O₃ + 1/2Fe₂O₃ values of Oxisols do not approach this critical level.

If the association of high m values with andic materials and low m values with oxic materials, discussed previously, holds true, then soil in the Andisol-Oxisol continuum will exhibit the relationships illustrated in Figure 4.1. Stated simply, the phosphate retention and level of Al₂O₃ + 1/2Fe₂O₃ should increase and bulk density values should decrease as m increases.

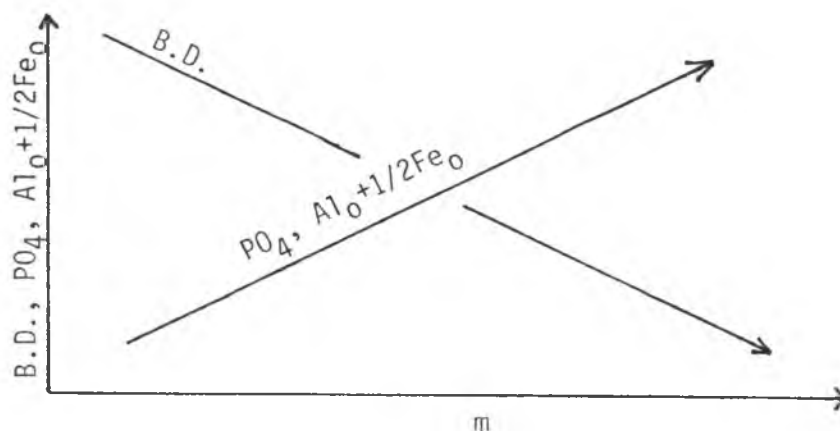


Fig. 4.1. Expected relationships between the variable charge indicator m , phosphate retention, $Al_0 + 1/2Fe_0$, and bulk density.

Figures 4.2 and 4.3 show that these soils exhibit the expected trends in m values with regards to phosphate retention and bulk density, respectively. The relationship between $Al_0 + 1/2Fe_0$ and the variable charge indicator is illustrated in Figure 4.4. Although there is not enough data to be sure, it appears that $Al_0 + 1/2Fe_0$ increases as m increases.

Kimble and Eswaran (1988) provided evidence that under certain conditions, Oxisols may exhibit the high phosphate retention and low bulk density values typical of Andisols. High phosphate retentions may occur in Oxisols when the ZPNC of the soil is greater than 4.5. Under these conditions, soil acidity may equilibrate at the ZPNC, and the amount of exchangeable cations will be negligible and the phosphorus fixation potential will be

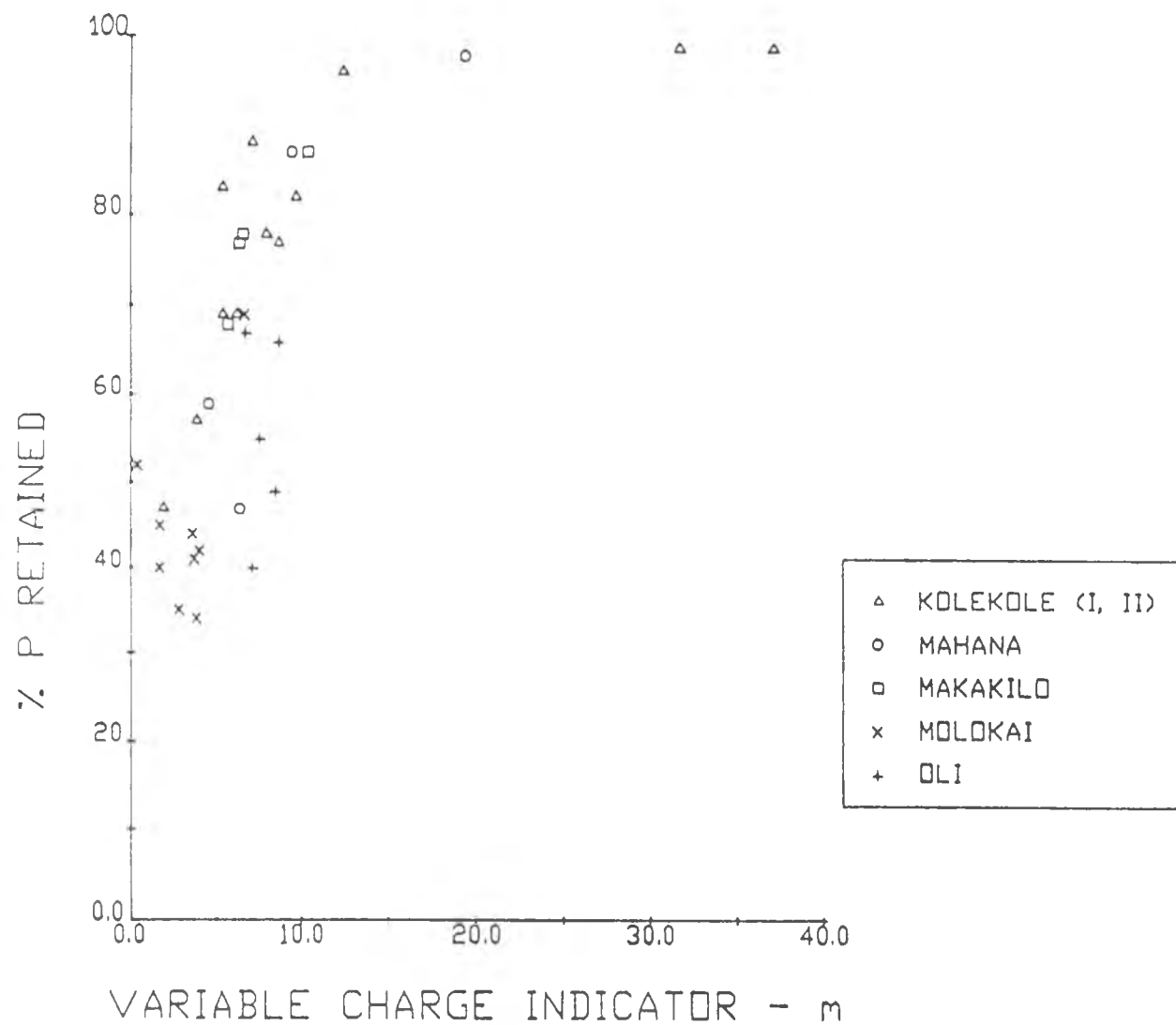


Fig. 4.2. Relationship between the variable charge indicator m and phosphate retention

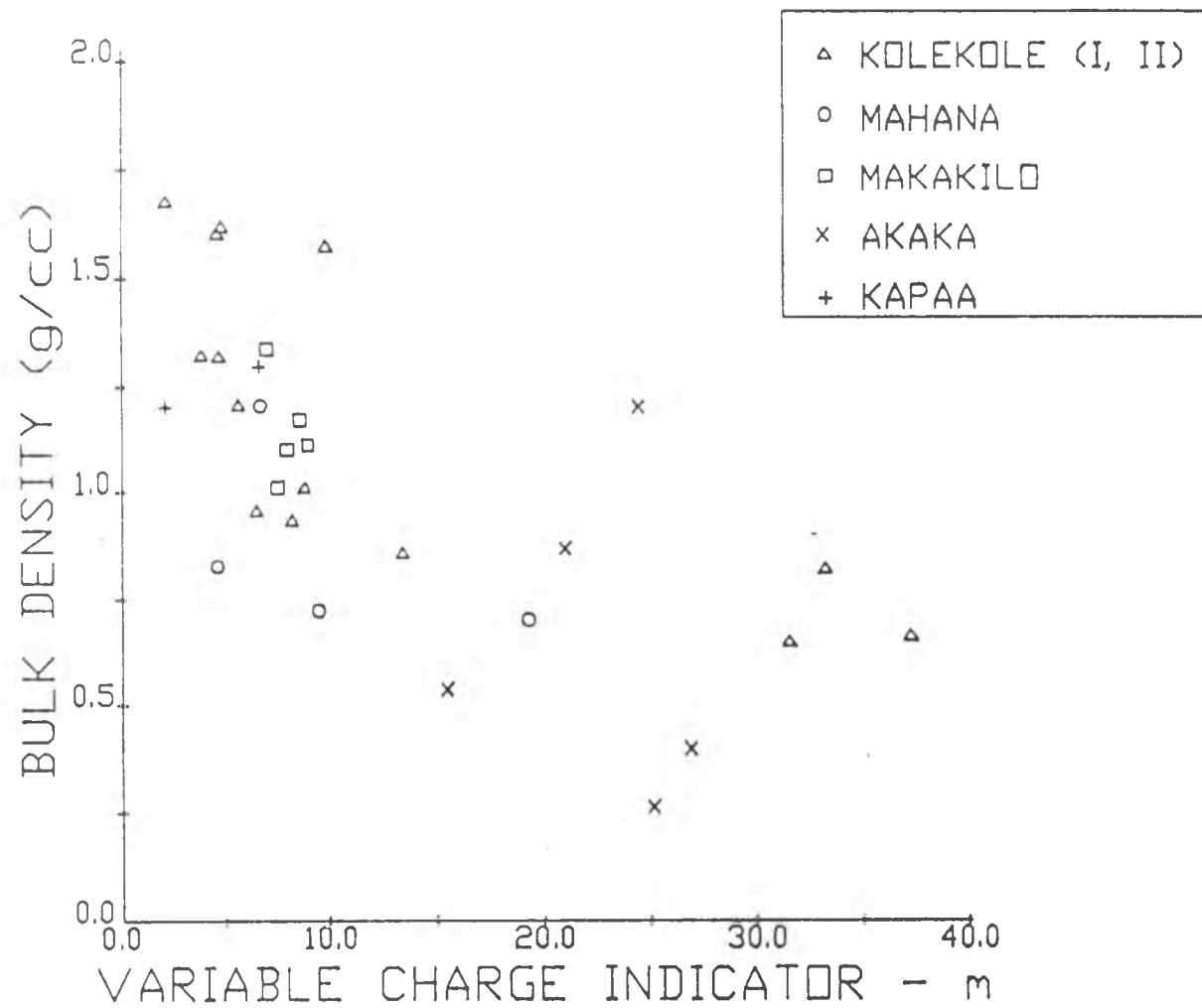


Fig. 4.3. Relationship between the variable charge indicator m and bulk density.

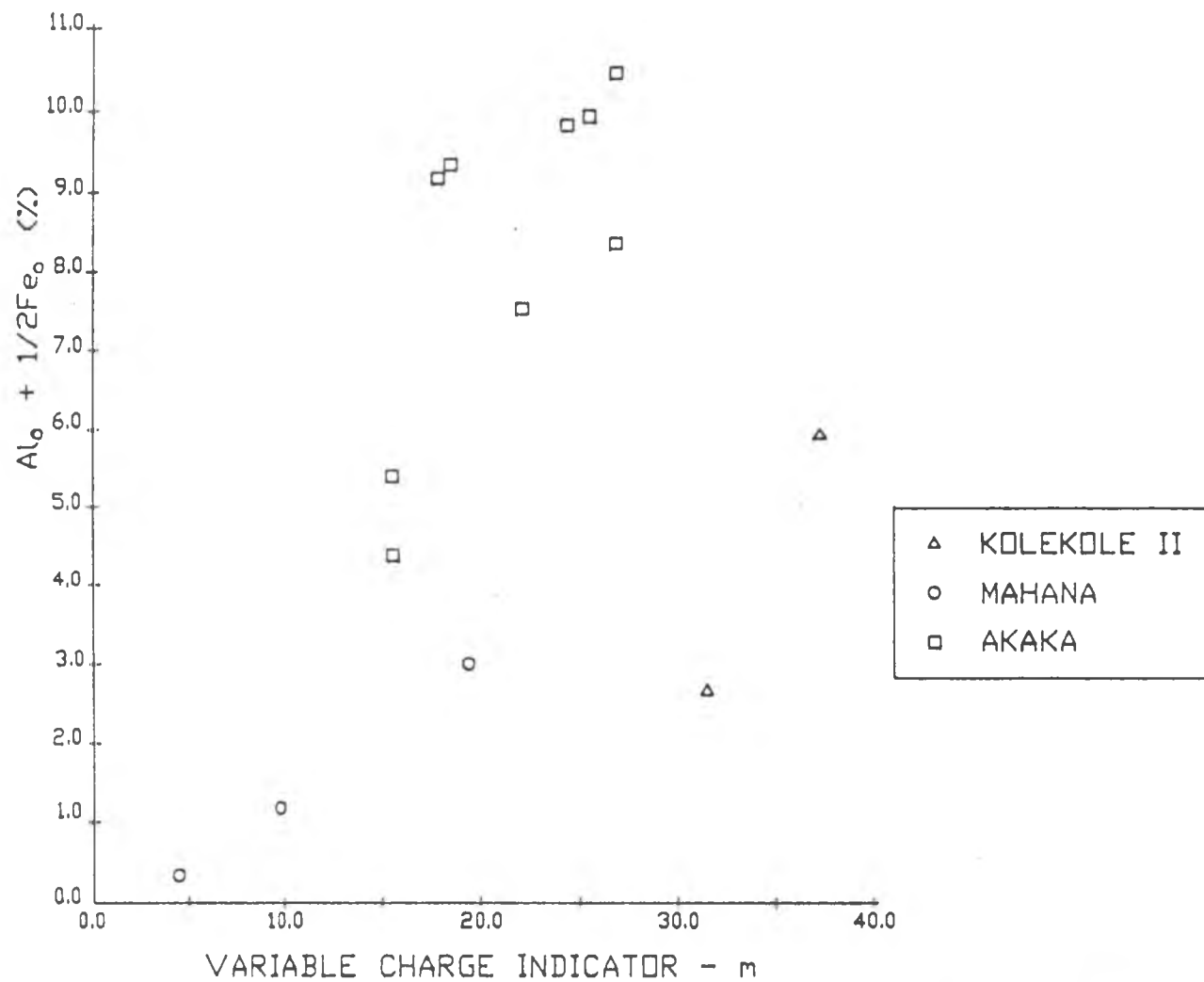


Fig. 4.4. Relationship between the variable charge indicator m and $AlO + 1/2FeO$.

high (van Wambeke et al., 1983). Kimble and Eswaran, therefore, concluded that neither of these properties should be used by itself to distinguish Andisols from Oxisols. The results of this study suggest that both phosphate retention and bulk density can be used with some success to refine the andic-oxic soil category into three subcategories. These are: near-andic, andic-oxic, and near-oxic.

Figure 4.5 shows the same data that were presented in Figure 4.2, with the addition of vertical lines representing the two "andic-oxic" isolating boundaries ($m = 5.5$ and $m = 12$). In addition, a horizontal line representing minimum phosphate retention for more finely textured Andisols, which equals 85 percent, has been included. A second horizontal line representing the maximum phosphate retention for the Oxisols encountered in this study, equalling 62 percent, has also been included. These boundaries were set after studying the data in Table 4.2, 4.3, and 4.4. The 62 percent value was obtained by taking the average of the two highest phosphate retention values of 55 and 66 percent exhibited by the oxic horizons. The three subcategories of "andic-oxic" material are thus established by these boundaries and labelled in Figure 4.5.

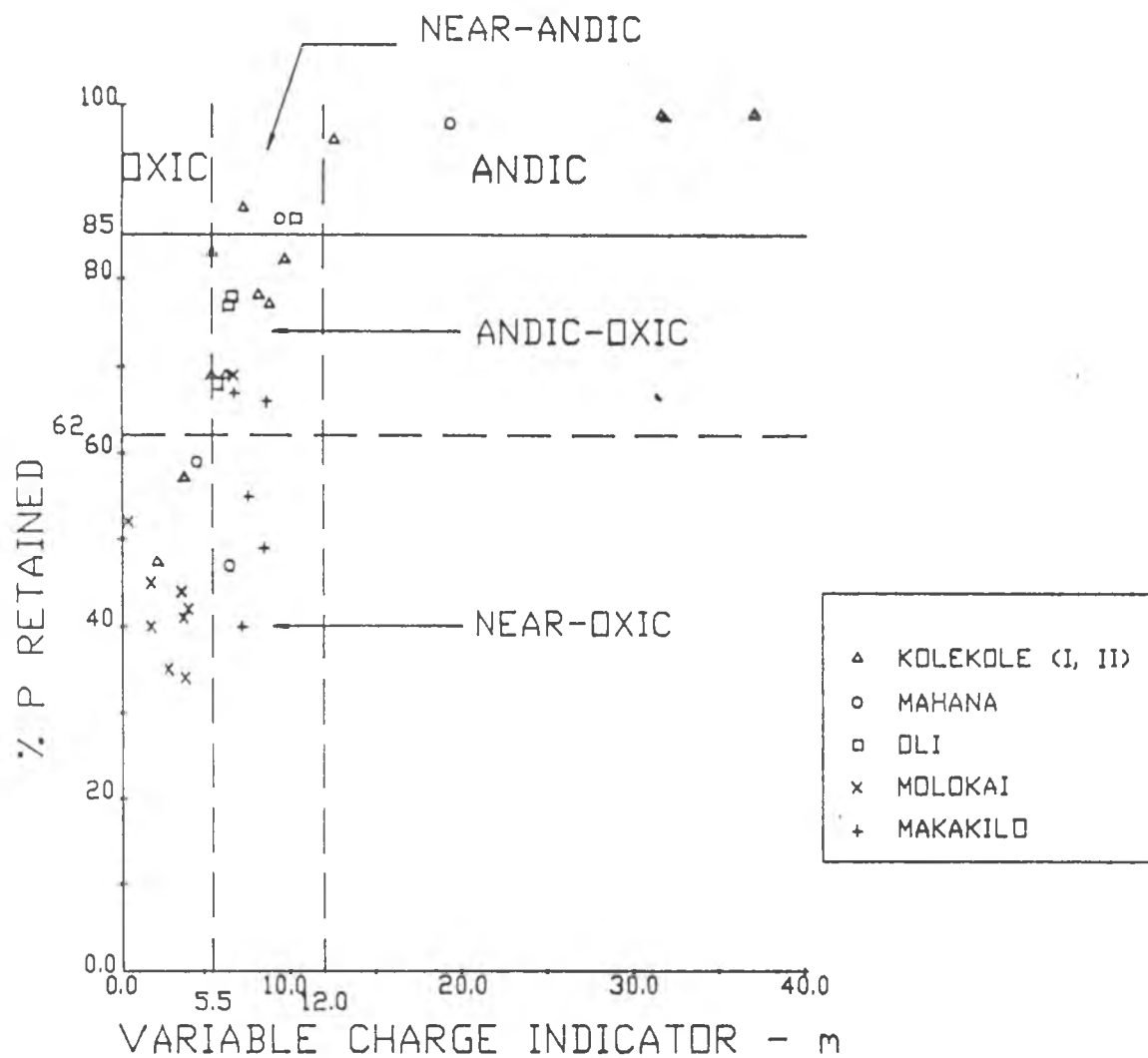


Fig. 4.5. Relationship between the variable charge indicator m and phosphate retention, with andic-oxic boundaries.

A similar method was used to establish boundaries for bulk density. The results are presented in Fig. 4.6. Again, the two vertical m values at 5.5 and 12.0 separate the andic-oxic soils. One horizontal line, representing 0.9 g cm^{-3} bulk density separates near-andic soils from other soils with both andic and oxic characteristics. The second horizontal line at 1.25 g cm^{-3} bulk density separates the near-oxic soils from other soils with both andic and oxic characteristics.

The various soil horizons may be placed in three groups based on the m values reported in Table 4.4, and the bulk density and phosphate retention boundaries established in Figures 4.5 and 4.6. The groupings of each horizon are listed in Table 4.5. Both phosphate retention and bulk density values were available for 16 horizons. Of these 16 horizons, 10 have similar separation for both phosphate retention and bulk density. The classifications of the remaining six horizons are not in agreement. These exceptions occur in the Kolekole and Mahana (Oahu) profiles.

The designations in Table 4.5 illustrate the variation in chemical and physical properties which occur both among horizons in a profile and between profiles in the same soil series. For example, the Mahana (Kauai) soil shows a decrease in oxic characteristics with depth.

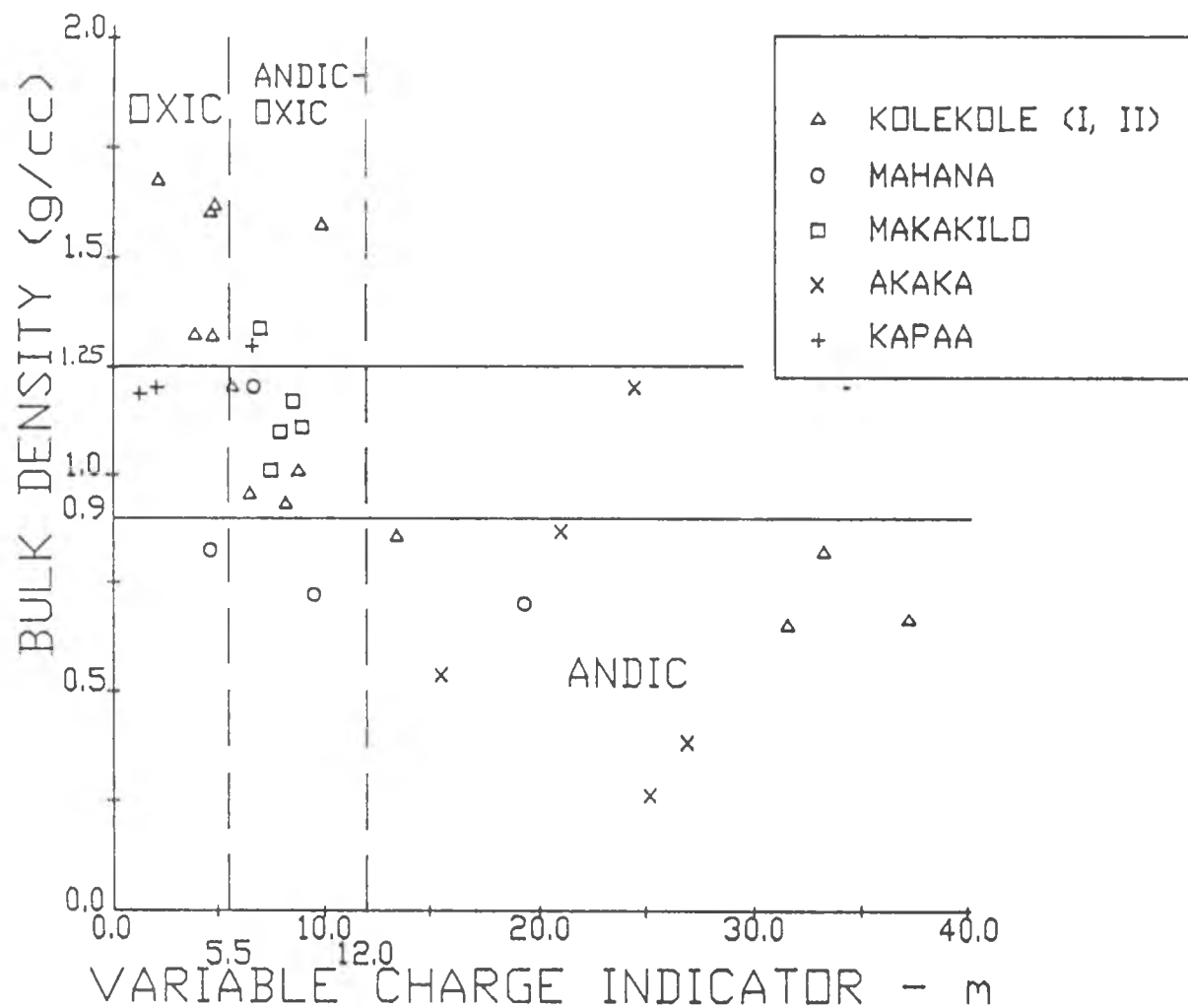


Fig. 4.6. Relationship between the variable charge indicator m and bulk-density, with andic-oxic boundaries.

The Mahana (Oahu) soil, which was mapped as a steep, eroded phase of the Mahana series, however, is uniformly andic-oxic and the differences in chemical properties and mineralogy between horizons are small (Tables 4.2 and 4.3). These results appear to indicate that the Mahana (Oahu) soil is less weathered than the Mahana (Kauai) soil and reflect an increased content of amorphous materials in the mineralogy and chemical properties in the latter soil.

The two Kolekole soils illustrate the variation in characteristics within a profile. The Kolekole I soil is andic-oxic in the surface but varies from oxic to andic-oxic to near-andic in the subsoil. The Kolekole II soil is andic-oxic in the surface but andic in much of the subsoil and oxic at depth. These variations reflect not only differences in weathering but also changes in parent material which are evident in the Kolekole profiles.

Table 4.5. Grouping of soil horizons into andic, andic-oxic, and oxic groups (based on m values (Table 4.4), and bulk density and phosphate retention boundaries).

Soil	Horizon	Ranking (BD / PO ₄)
Akaka	Ap1	ANDIC
	Ap2	ANDIC
	Bw1	ANDIC
	Bw2	ANDIC
	Bw3	ANDIC
	Bw4	ANDIC
	Bw5	ANDIC
	BC	ANDIC
Kapaa	Ap	OXIC
	Bo1	OXIC
	Bo2	OXIC
	Bo3	OXIC
	Bo4	OXIC
	Bo5	OXIC
Oli	A	NO DATA / ANDIC-OXIC
	Bw1	NO DATA / ANDIC-OXIC
	Bw2	NO DATA / ANDIC-OXIC
	Bw3	NO DATA / ANDIC-OXIC
Mahana (Kauai)	A1	NO DATA / NEAR-OXIC
	A2	NO DATA / OXIC
	Bw1	NO DATA / NEAR-ANDIC
	Bw2	NO DATA / ANDIC
	Bw3	NO DATA
Mahana (Oahu)	A1	ANDIC-OXIC / NEAR-OXIC
	A2	ANDIC-OXIC / NEAR-OXIC
	Bw1	ANDIC-OXIC / NEAR-OXIC
	Bw2	ANDIC-OXIC / NEAR-OXIC
	Bw3	NEAR-OXIC / ANDIC-OXIC

Continued on next page

Table 4.5 (Continued). Grouping of soil horizons into andic, andic-oxic, and oxic groups (based on m values (Table 4.4), and bulk density and phosphate retention boundaries).

Soil	Horizon	Ranking (BD / PO ₄)
Kolekole I	Ap1	NO DATA / ANDIC-OXIC
	Ap2	ANDIC-OXIC / ANDIC-OXIC
	Bw1	ANDIC-OXIC / ANDIC-OXIC
	Bw2	OXIC / OXIC
	Bw3	ANDIC-OXIC / ANDIC-OXIC
	2Bw1	ANDIC-OXIC / NEAR-ANDIC
	2Bw2	NEAR-ANDIC / NEAR-ANDIC
	3BC	OXIC / OXIC
Kolekole II	A1	OXIC / NO DATA
	A2	ANDIC-OXIC / ANDIC-OXIC
	2Bw1	ANDIC / ANDIC
	2Bw2	ANDIC / NO DATA
	2Bw3	ANDIC / ANDIC
	3Bct1	NEAR-OXIC / ANDIC-OXIC
	3Bct2	OXIC / NO DATA
	3Bct3	OXIC / NO DATA
Molokai	Ap1	NO DATA / OXIC
	Ap2	NO DATA / OXIC
	Bo1	NO DATA / OXIC
	Bo2	NO DATA / OXIC
	Bo3	NO DATA / OXIC
	Bo4	NO DATA / OXIC
	Bo5	NO DATA / OXIC
	Bo6	NO DATA / OXIC

The Classification of the Soils

Finally, the laboratory data are used to classify the soils that were used in this study. The tentative taxonomic names, based on the latest revision to Soil Taxonomy (Soil Survey Staff, 1975), are listed in Table 4.6.

Table 4.6. Tentative taxonomic classification of the soils

Soil	Former Classification	New Classification
Akaka	Typic Hydrandept	Acrudoxic Hydrudand
Kapaa	Typic Gibbsihumox	Anionic Acrudox
Kolekole I	Ustoxic Humitropept	Ustoxic Humitropept
Kolekole II	Ustoxic Humitropept	Dystric Haplustand
Mahana (Kauai)	Typic Acrohumox	Andic Dystropept
Mahana (Oahu)	Typic Acrohumox	Tropept
Molokai	Typic Torrox	Rhodic Eustrustox
Oli	Oxic Dystrandep	Andic Dystropept

The change in the classification of the Akaka and Kapaa soil series was expected because of the revisions in Soil Taxonomy. The classification of the Molokai profile also reflects the revisions. The classification of the Kolekole I soil remains unchanged. The classification of Kolekole II soil, however, has changed. This soil is now

an Andisol because of the andic soil properties in the 2Bw horizons which extend from 60 to 118 cm.

The Mahana (Kauai) soil is an Inceptisol rather than an Oxisol because of the absence of an oxic horizon. Because of low base saturation, this soil is further classified as a Dystropept. Because of the near-andic properties in the Bw1 horizon and the andic properties in the Bw2 horizon, it is finally classified as an Andic Dystropept.

The Oli soil is also classified as an Andic Dystropept. The change from Oxic Dystrandept to Andic Dystropept reflects the changes in the Inceptisol order caused by the establishment of a separate order, the Andisols, for soils derived from volcanic ash parent material.

The groupings listed in Table 4.5 correlate well with the actual taxonomic classifications of the soils analyzed in this study. Every horizon of the Akaka soil, an Andisol, fell in the andic group. Similarly, every horizon of the Kapaa and Molokai soils, both Oxisols, fell in the oxic group. The horizons of the Kolekole I and II, Mahana (Kauai), Mahana (Oahu), and Oli soils fell in the intermediate groups of near-andic, andic-oxic, and near-oxic. With the exception of the Kolekole II soil, these soils were classified as Andic or Ustoxic subgroups of Inceptisols. This outcome suggests that the m value, used

in conjunction with bulk density and phosphate retention values, may be used to make an educated guess as to the correct taxonomic classification of an ash-influenced soil.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Published and unpublished data were used to study the andic, oxic, and andic-oxic properties of selected soils of Hawaii. They included a soil with definite andic properties (Akaka) and a soil with definite oxic horizon (Kapaa). Others were thought to have contributions of volcanic ash and have andic-oxic properties (Oli, Kolekole, Mahana, and Molokai).

The data for the Oli, Kolekole, and Mahana soils supports the hypothesis that these soils represent volcanic-ash influenced soil in transition between Andisols and Oxisols. The results of the analysis of the Molokai soil did not support this conclusion.

A variable charge indicator m was developed in this study using CEC (NH_4OAc , pH 7) and ECEC values at field pH (1:1 H_2O) to correlate and to test the soils with andic, oxic, and andic-oxic properties. The grouping of the soils was possible not only using the variable charge indicator m but also using phosphate retention and bulk density. Reliability of the andic-oxic groups may be increased by using $\text{Al}_\text{O} + 1/2\text{Fe}_\text{O}$ values as supporting data but more such data are necessary.

APPENDIX 1

Narrative Description of the Soil Series

Akaka Series

The Akaka series consist of moderately well drained silty clay loams that formed in volcanic ash. It occurs on uplands on the island of Hawaii.

The soil was sampled by the SCS along the edge of a forest about 1.8 miles directly southwest of Akaka Falls. Approximate latitude and longitude of this location is 19 degrees 50 minutes 47 seconds north latitude and 155 degrees 09 minutes 58 seconds west longitude. Elevation at the site is 527 m above sea level. Average annual precipitation is 6600 mm; the mean annual soil temperature varies between 13.3° and 15° C. This soil is identified by soil survey lab sample number S87-HI-001-005.

This profile has a surface layer of dark reddish-brown silty clay loam about 43 cm thick. This layer is strongly acid. The upper part of this layer has strong coarse to fine granular structure; structure in the lower part is weak subangular blocky. The subsoil is reddish-brown to dark reddish-brown silty clay loam, about 110 cm thick. This layer has weak to moderate subangular blocky structure and is strongly acid to medium acid. Many gelatin-like coatings are found on the faces of peds in

the subsoil. This soil dehydrates irreversibly into fine gravel-size aggregates and is weakly smeary to smeary throughout the profile.

Permeability of the Akaka silty clay loam with 10 to 20 percent slopes is rapid; runoff is medium and the erosion hazard is slight. Much of this phase is used for sugarcane cultivation.

Kapaa Series

The Kapaa series consists of well-drained soils on uplands on the islands of Kauai and Oahu. Typically, these soils weathered in material weathered from basic igneous rock. The results of the analysis of the representative profile for the Kapaa silty clay, 3 to 8 percent slopes phase were used in this study; this phase formed in volcanic ejecta (Foote et al., 1972).

The sample was taken by the SCS on the island of Kauai, at 22 degrees 02 minutes 42 seconds north latitude and 159 degrees 23 minutes and 31 seconds west longitude. Elevation at this site is 117 m (390 feet). Average annual precipitation is 2250 mm and mean annual temperature is 23⁰ C. The established vegetation is cultivated sugarcane. The results of the chemical and physical analyses of this pedon (S65Ha-2-4) are published in Soil Survey Investigations Report No. 29 (Soil Conservation Service, 1976).

The surface layer is dark yellowish-brown silty clay about 36 cm thick; this layer is strongly acid. The subsoil, about 117 cm thick, is yellowish-red and reddish-brown silty clay that has subangular blocky structure. The substratum is soft, weathered rock. The surface layer and the upper part of the subsoil contain less gibbsite than is typical. The subsoil is medium acid to very strongly acid.

Permeability of this soil is moderately rapid. Runoff is slow and the erosion hazard is slight.

Oli Series

The Oli series consists of well-drained, moderately deep to deep soils on uplands. It is found on the islands of Molokai and Maui, in addition to Kauai. According to Foote et al. (1973), the soils developed in volcanic ash deposited over basic igneous rock. This series occurs at elevations ranging from 300 to 685 m. The annual rainfall amounts to 762 to 1016 mm and falls mostly in the months between November and April. The mean annual soil temperature is 21⁰ C (Foote et al., 1972). The sample was taken from a pedon of the Oli silt loam, 10 to 30 percent slopes phase. This phase occupies uplands that are dissected by many gulches.

The sample site is located on a ridge adjacent to Kamokala Ridge, at the side of a secondary road off of

Highway 55 (see Foote et al., 1973, map sheet 3).

Approximate latitude and longitude of this site is 22 degrees 03 minutes 30 seconds north latitude, 159 degrees 40 minutes west longitude.

In a representative profile, the surface layer, about 33 cm thick, is dark-brown silt loam and loam. The subsoil, about 43 cm thick, is dark-brown silt loam that has prismatic and subangular blocky structure. A lithologic discontinuity appears at roughly 76 cm (30 inches); below this depth is slightly weathered hard rock which is penetrated by roots in places (Foote et al., 1972).

The soil is strongly acid to very strongly acid. It has moderately rapid permeability and medium runoff. The erosion hazard is moderate to severe due to its very friable and powdery consistency. The available water capacity is about 1.5 inches per foot of soil (Foote et al., 1973).

Mahana Series

The Mahana series consists of well-drained soils on uplands on the islands of Kauai and Oahu. Samples were collected from sites on both islands. These soils developed in volcanic ash (Foote et al., 1973). This conclusion was originally suggested by the work of Walker et al. (1969), whose study found strong evidence that the

soil developed in pyroclastic materials of post erosional origin.

The pedon from Kauai which was sampled for this study was also used in previous research by Montagne (1970). This work identifies the pedon as a member of the Naiwa series, but this classification was made before correlation and completion of the final soil survey. The published soil survey identifies this pedon as a member of the Mahana silt loam, 20 to 35 percent slopes, eroded phase (Foote et al., 1972).

The sample site is just southeast of the Kekaha-Kokee road, "where this road first closely approached the Waimea Canyon, just northeast of the 2319 feet bench mark (Montagne, 1970)." The pedon was situated on a gentle ($< 15^{\circ}$) slope, running NE-SW. This slope is cut through by Waimea Canyon at a point about 1 mile NE of the pedon. Geographically, the pedon is located at approximately 159 degrees 40 minutes west longitude and 22 degrees 01 minutes north latitude (Foote et al., 1972, map sheet 4). Annual rainfall at the site is roughly 1525 mm; the climate has pronounced wet and dry seasons (Montagne, 1970). Mean annual temperature in the area is 19.4° C.

The following profile description is taken from Montagne (1970):

"(The profile has) a vegetative cover of small shrubs. Roots were abundant in the upper 8 inches of the profile and gradually decreased in number going downwards, disappearing at around 30 inches of depth. The soil was friable from the surface down to the massive horizon at 35-inch depth The layer from 16 to 35-inch depth was extremely friable."

The 35 inch (89 cm) depth marks a lithologic discontinuity and no soil was sampled below this depth.

Montagne (1970) also reports that in some places, the friable surface horizons had become indurated and the bulk density of these horizons had increased as a result of removal of vegetation by overgrazing and burning. The crust, although massive, could be crumbled into smaller aggregates and subsequently into fine dust by exerting some effort.

The soil survey reports that runoff is rapid and erosion hazard very severe for this phase of the Mahana series (Foote et al., 1972). Permeability and available water holding capacity were not reported.

The second Mahana pedon was sampled above Makakilo, on the southern end of the Waianae Range, overlooking the Ewa Plain of Oahu. This site, an abandoned pasture, is located approximately 30 m from a water tank above the community of Makakilo, and is in the immediate vicinity of

three volcanic cones, Puu Makakilo, Puu Palailai, and Puu Kapolei.

The surface horizon, 8 cm in depth, was dark reddish brown fine sandy loam. This layer had moderate granular structure, with many very fine roots. Consistency was friable and smeary. This surface horizon, as well as the immediate subsoil (8 to 34 cm) exhibited characteristics, such as fine "fluffy" texture and low bulk density, typical of ash-derived soils.

The subsoil (8 to 34 cm) was dusky red loam in the upper portion and dark reddish brown loam in the lower portion. The layer had fine medium and coarse subangular blocky structure and the strength of expression decreased with depth. Very fine and fine roots and pores were common and charred fine roots were visible in the lower portion of this layer. Consistency was very friable to friable, slightly sticky, slightly plastic and smeary throughout.

A lithologic discontinuity marked the boundary at 34 cm. The soil below this depth was dark reddish brown (hue of 5YR) loam. The upper part (34 to 58 cm) had moderate fine medium and coarse subangular blocky structure. Very fine and fine roots and pores were common and few medium and coarse roots were present, mostly in the first 10 cm. A root mat marked the boundary between this horizon and

the lower horizon. Consistency was very friable, slightly sticky, slightly plastic and smeary.

The lower part (58 to 84 cm) of this pedon was also dark reddish brown loam. This soil felt more gritty than the horizon above, possibly due to the presence of many sand sized particles. Structure of this horizon was weak medium subangular blocky breaking to strong very fine and fine subangular blocky. Very fine roots and pores were common; many charred roots were found in this horizon. Root mats with wavy, horizontal orientation occurred at depths of 62 and 77 cm. Consistency was friable, sticky and plastic, and slightly smeary.

Kolekole Series

This series consists of well-drained soils developed in volcanic ash mixed with old gravelly alluvium. It occurs on uplands on the windward slopes of the Waianae Range on the island of Oahu. Elevations range from 152 to 366 m. The annual rainfall amounts to 889 to 1270 mm, most of which occurs between November and April, and the mean annual soil temperature is 21.7° C (Foote et al., 1972).

Samples were taken from a pedon on the bank of a roadcut on Kunia Road, approximately 7.68 km from the Farrington Highway-Kunia Road junction, between the Hawaii Country Club and Kunia Camp. The sample site occurs on a

unit of the Kolekole silty clay loam, 1 to 6 percent slopes phase.

The surface layer is dark reddish-brown silty clay loam about 41 cm thick. A compact panlike layer, which restricts roots and is marked by the presence of root mats, occurs at a depth of 58 cm. This layer forms an abrupt horizon with the upper part of the B horizon. The subsoil is about 100 cm thick and consists of reddish-brown silty clay loam and silty clay with subangular and angular blocky structure. A lithologic discontinuity appears at 141 cm; the soil below this boundary is marked by browner colors, somewhat massive structure and heavier specific gravity (according to field observations). The soil survey describes the substratum as "old gravelly alluvium," (Foote et al., 1972).

The soil is extremely acid to strongly acid in the surface layer and medium acid to very strongly acid in the subsoil. Permeability is moderately rapid to the panlike layer and moderate in the compact subsoil. Runoff is slow, and the erosion hazard is slight. The available water capacity is about 1.3 inches per foot of soil.

The soil survey (Foote et al., 1972) reports that the greatest variation in the series is the depth to the panlike layer. The depth to this layer is typically 610 to 1016 mm but ranges from 381 to 1270 mm. The amount of highly weathered rock fragments varies considerably within

short distances but normally makes up between 30 and 40 percent of the volume (Foote et al., 1972).

Molokai Series

The Molokai series consists of well-drained silty clay loams on uplands on the islands of Maui, Lanai, Molokai, and Oahu. The published soil survey describes the parent material as "material weathered from basic igneous rock," (Foote et al., 1972).

The soil was sampled from the northern side of a road bank on land cropped to sugarcane by the Oahu Sugar Company. The road is located 2.72 km north of the junction of Farrington Highway and Kunia Road. This site was also used in thesis research conducted by Nuanchavee Yaibuathes (1969). Elevation at this location is 457.3 m; mean annual temperature is 22.8° C. Annual rainfall ranges from 375 to 625 mm, (Yaibuathes, 1969).

The surface layer (Ap1), about 30 cm thick, consists of dark reddish-brown silty clay loam that has very weak coarse granular structure. It is friable, with many roots and interstitial pores. This layer also has many fine black concretions, assumed to be composed of iron and manganese and it shows strong effervescence with hydrogen peroxide.

The Ap2 horizon (30 to 83 cm) is dark red silty clay which has weak coarse prismatic structure. It has friable

to firm consistency. Roots, tubular pores and concretions are common. This horizon also exhibits strong effervescence with hydrogen peroxide.

The remainder of the subsoil is roughly 50 cm thick. It consists of dark red silty clay loam in the upper 30 cm and dark red silty clay in the lower portion. Structure is weak to moderate blocky in the upper part and strong angular and subangular blocky at depth. Roots and pores are few to very few. The presence of iron-manganese concretions decreases with depth. Prominent thin patchy clay films are described on peds in the lower 20 cm.

This site occurs on a unit of Molokai silty clay loam, 0 to 3 percent slopes. Permeability for this phase of the Molokai series is moderate; runoff is slow and the erosion hazard is slight. The available water capacity is roughly 1.3 inches per foot of soil (Foote et al., 1972).

APPENDIX 2

GEOLOGY OF THE HAWAIIAN ISLANDS

The Hawaiian Islands are a chain of shield-shaped basaltic domes built over a fissure 2560 km long in the ocean floor (Stearns, 1967). The chain stretches from southeast to northwest, between $154^{\circ} 40'$ and $178^{\circ} 75'$ west longitude and $18^{\circ} 54'$ and $28^{\circ} 15'$ north latitude.

According to the "hot spot" theory, the islands were formed as the Pacific plate on which they sit moved over a source of heat, or "hot spot," deep within the earth. The hot spot continually generates the magma which feeds the Hawaiian volcanoes. The theory proposes that the hot spot has remained relatively stationary for millions of years, while the Pacific plate has gradually moved northwest, resulting in the linear chain of volcanic islands (Macdonald et al., 1983).

Hawaiian volcanoes exhibit a unique eruption behavior which has become known as Hawaiian-type eruptions. Such eruptions are gentle and involve almost no explosion because the lava is fluid and contains very little gas (Macdonald et al., 1983). The lava fountains and jets which are often reported are streams of magma flowing under pressure and are not explosive. The results of this type of eruption are the two types of lava flow, aa and

pahoehoe. The hydromagmatic or phreatomagmatic eruptions which produce ash or tephra are relatively rare (Stearns, 1967).

Analysis of the chemical composition of the magma of the Hawaiian volcanoes reveals that they are tholeiitic in nature (Macdonald and Katsura, 1964). Such flows are relatively rich in silica and poor in sodium and potassium. In addition, the flows contain pigeonite, a pyroxene containing little Ca or Al. Some of the later flows of these volcanoes (for example, the upper member of the Waianae Volcanic series) produced alkalic olivine basalt, a rock which is comparatively poor in silica and rich in sodium and potassium. Such rocks also contain augite, a pyroxene containing Ca and Al. The process of magmatic differentiation, in which early-forming crystals become separated from the remaining melt and leave a liquid residue with a composition different from that of the original melt, explains how a tholeiitic magma can produce alkalic rocks such as hawaiite (Macdonald and Katsura, 1964).

Although soil scientists have described 91 soil series with volcanic ash parent material in the state of Hawaii, geologists have mapped areas of deposition of volcanic ash only on the island of Hawaii. Geologists, however, have recorded evidences of "thin" ash falls on Oahu and Kauai. On Oahu, geologists found thin layers of

ashy soils sandwiched between the lava flows of the Waianae cinder cones and the upper member of the Waianae Volcanic Series. In addition, pillow lavas found in Waimea Canyon on the island of Kauai are overlain by several centimeters of palagonitized vitric ash. Ash falls are also exposed in a valley at the base of the Wailua Falls (Macdonald et al., 1983).

There are two possible explanations for the lack of agreement between soils scientists and geologists. First, ash falls which are geologically "thin" (e.g., 1 to 25 m) may not have been mapped due to the vertical scale of geologic mapping. Such a deposit, however, would be sufficient for soil genesis. Alternatively, ash deposits may not have been recognized as such by geologists due to the actions and processes of soil formation.

Geology of Oahu

Soils on the eastern footslopes of the Waianae Range, such as the Mahana and Kolekole series, are recognized by soil scientists as having formed in volcanic ash. These soils are classified as Inceptisols. The highly weathered soils of the Schofield Plateau, which are mostly Oxisols and Ultisols, have generally been characterized as residual soils developed in basalt (Gavenda, 1989; Foote et al., 1972). The Molokai series is an Oxisol found extensively in this area.

Along with the Koolau Volcano, the Waianae Volcano, formed the volcanic doublet island of Oahu. The Waianae Range, the highly eroded remnant of the ancient shield volcano, is the eldest of the two. The Schofield Plateau, the gently sloping surface which links the two ranges, was formed as the lava flows from the Koolau volcano banked against the already-eroded slope of the Waianae volcano (Macdonald et al., 1983).

The Waianae Volcanic Series consists of three members, erupted in Tertiary and possibly early Pleistocene (Stearns, 1967). The oldest Waianae lavas have been dated at 3.8 million years using potassium-argon dating methods (McDougall, 1964, cited in Gavenda, 1989). The youngest of these lavas have been dated at 2.2 million years (McDougall, 1964; Funkhouser, 1968; Doell and Dalrymple, 1973, cited in Gavenda, 1989). The petrography and petrology of the Waianae Volcanics were reviewed by Macdonald (1940).

The lower member of the Waianae Volcanic Series consists of the thin bedded tholeiitic pahoehoe lava flows and pyroclastic rocks that build the Waianae shield (Macdonald et al., 1983; Stearns, 1967).

The middle member is separated from the lower member by an angular unconformity and talus breccia in most places and by an erosional unconformity in a few places (Stearns, 1967). This member is roughly 610 m thick and

"closely resembles the lower ones except that the later beds contain more aa," (Stearns, 1967). It consists of the rocks that accumulated in the caldera of the Waianae volcano. Although the bottom flows of the member are tholeiitic, alkalic basalts begin to appear near the top. This change is attributed to fractional differentiation of the magma (Macdonald and Katsura, 1964).

The upper member is a veneer of lava flows which covered the entire top of the shield late in its history (Macdonald et al., 1983). These flows were largely hawaiite with lesser amounts of alkalic olivine basalt (Macdonald et al., 1983), and were "about 2300 feet thick ... mostly massive aa andesite flows which issued from cinder cones," (Stearns, 1967.)

Another volcanic stage ensued at some time during the mid-Pleistocene, after much erosion of both the Waianae and Koolau shield volcanoes. Secondary eruptions which occurred near the caldera of the Waianae volcano produced a flow of alkalic olivine basalt in Kolekole Pass; thus flows of this lithologic unit are called the Kolekole Volcanics. Because the flow rests on alluvium which had accumulated in a deep stream cut valley, this eruption was certainly post-erosional (Macdonald et al., 1983).

A row of five cinder cones, Puu Kuua, Puu Kapuai, Puu Makakilo, Puu Palailai, and Puu Kapolei, occurs along the lower south border of the Waianae Range. They are

composed of a varied mixture of cinder, splatter, and lava flows. Previously, these cones had been included in the Waianae Volcanic Series (Macdonald et al., 1983; Stearns, 1967). A recent reevaluation of the stratigraphy of the Waianae Range reveals that these cinder cones also belong to the Kolekole Volcanics unit (Sinton, 1986). The stratigraphic relationships presented in this work indicate that the cinder deposits are post-erosional and probably Pleistocene in age although the isotopic age of the Kolekole Volcanics is not known. It seems reasonable that one or more of these secondary eruptions could have produced pyroclastics which mantled the Wahiawa Basin (Gavenda, 1989).

As previously stated, the Schofield Plateau is the gently sloping surface formed by coalescence of flows of the Koolau volcano against the eroded slopes of the Waianae volcano. Geologists have mapped the area as lava flows of the Koolau Volcanic Series. The soils of this area, mostly Oxisols and Ultisols, have generally been characterized as residual soils developed in basalt (Gavenda, 1989; Foote et al., 1972).

A recent study proposes a different sequence of events in the landscape evolution and soil development in central Oahu: "(1) erosion of Koolau and Waianae Volcanos; (2) formation of soils in residual basalt; (3) formation of alluvial fans at the base of the Waianae Range; (4)

development of soils in the Waianae alluvial fans; (5) basin-wide truncation of soil profiles and concurrent downcutting of stream channels; (6) deposition of one or more volcanic ash layers, possibly separated by erosional periods; (7) formation of soils in the volcanic ash and the concurrent accumulation of tropospheric dust from mainland Asia; and (8) further downcutting of stream channels but stabilization of interfluve surfaces as evidenced by the accumulation of tropospheric dust¹," (Gavenda, 1989).

Gavenda (1989) observed a discontinuity in all but one profile along a transect from the Inceptisols of the Waianae Range to the Oxisols and Ultisols of the Koolau Range. The stratigraphic relationships between the discontinuity and landforms suggest that the discontinuity is an erosion surface and that soil horizons above this surface formed in a single layer that mantles all geomorphic surfaces. Mineralogical analysis of the soils shows very low amounts of magnetite and ilmenite in the horizons above the discontinuity but higher amounts below the discontinuity. These two resistant primary minerals are found in only trace amounts in pyroclastic deposits of the Honolulu Volcanics² and in the volcanic ash-derived

¹ The accumulation of tropospheric dust explains the presence of quartz in Hawaiian soils and was documented by the work of Rex and his coworkers (1969).

² This lithologic unit represents post-erosional eruptions of a rejuvenated stage of the Koolau Volcano.

Kolekole series. Based on these two independent lines of evidence, Gavenda concludes that the highly weathered B horizons above the discontinuity in the Oxisols and Ultisols developed in volcanic ash, while the A horizons developed in the tropospheric dust (Gavenda, 1989). Gavenda's work suggests that, despite previous conceptions of the geology, at least the B horizons of the Molokai soil used in this study are examples of an Oxisol which developed in volcanic ash.

Geology of Kauai

The island of Kauai consists of the deeply eroded remnant of one great shield volcano. Volcanics of a later period partly veneered these remnants (Macdonald et al., 1983). The largest caldera in the Hawaiian islands, roughly 15 to 20 kilometers across, was formed at the top of the shield. A fault-bounded trough called the Makaweli graben was formed when the southern flank of the shield collapsed.

The rocks which formed the Kauai shield volcano are named the Waimea Canyon Volcanic Series. A portion that built the main mass of the shield outside the caldera are called the Napali Formation. This formation consists of thin flows of tholeiitic basalt, olivine basalt, and oceanite pahoehoe and aa sloping gently outward in all directions from the summit area (Macdonald et al., 1983).

Both soil samples from Kauai were taken from sites bordering Waimea Canyon. The Mahana series was sampled just southeast of the Kekaha-Kokee road, "where this road first closely approached the Waimea Canyon, just northeast of the 2319 feet bench mark (Montagne, 1970)." A second sample, from a pedon of the Oli series, was taken from a site located on a ridge adjacent to Kamokala Ridge, at the side of a poorly developed road off of Highway 55. These sites are in the vicinity of known vents of the Koloa Volcanic Series. The vents represent a possible source of volcanic ash for soil formation, as cones of mixed splatter and cinder were built at these vents.

The Koloa lavas, like the Honolulu Volcanic Series and the Kolekole Volcanic Series on Oahu, represent a period of renewed volcanism. The chemical composition of the Koloa volcanics is also similar to that of the rejuvenated period rocks from Oahu. They range from alkalic olivine basalt through basanites to nephelinites and melilite nephelinites (Macdonald et al., 1983). The oldest of the Koloa lavas has been potassium-argon dated at 1.5 million years (Macdonald et al., 1983).

The Mahana sample site appears to be located on or near a finger of the Makaweli formation, in the upper portion of the Makaweli graben. This formation consists of predominantly tholeiitic lavas that accumulated in the graben. Alkalic olivine basalt and hawaiiite appear among

the latest flows. Because they were partly confined within a depression, Makaweli lavas are thicker and flatter than the Napali lavas.

In places at the upper end of the graben, the Makaweli lavas rest on, or are interfingered with, thick accumulations of cinder and ash. It is surmised that the cinder and ash were blown from lava fountains in the caldera or washed from the caldera region by streams and banked against the head wall of the graben (Macdonald et al., 1983). Along the lower portion of Waimea Canyon, layers of ash as much as a meter thick lie between the Makaweli lavas. Lava rests on 5 to 10 centimeters of baked red tuffaceous soil 150 meters west of the intake of the Kekaha ditch (Macdonald et al., 1983).

APPENDIX 3

FORMATION AND PEDOGENESIS OF ANDISOLS

Formation of Andisols

Andisols are characterized by the transition from unweathered to more weathered volcanic material. Although this transition is characteristic of some other orders, Andisols are unique in that the factors of soil formation, along with the pedogenic processes of humus accumulation and mineral weathering and transformation, give rise to short-range-order minerals. Under some conditions, these minerals achieve a stability that allows them to persist with no or only very slow further alteration over long periods. The stability of these minerals, along with their unique physical and chemical properties, is what sets Andisols apart from other soil orders.

As soil parent material, volcanic ejecta, especially volcanic ash and pumice, possess two important features. Because these materials are fine-grained or porous, they have large specific surface area. This quality enhances their interaction with the soil environment and accelerates weathering. In addition, volcanic ejecta often contains large amounts of non-crystalline volcanic glass and other weatherable minerals. A rapid weathering of volcanic ash and pumice, particularly under humid conditions and at well-drained sites, results in loss of

silica and "bases" by leaching and accumulation of Al and Fe in weathering products (Wada, 1985). These weathering products are primarily allophane, allophane-like constituents, opaline silica, imogolite, and Al- and Fe-humus complexes. Halloysite and 2:1 hydroxy-interlayered silicates may also be formed under certain conditions (Wada, 1985).

The silica content of Hawaiian lavas is generally less than 50% (Macdonald and Katsura, 1964). Under the classification system proposed by Shoji et al. (1975), the ash produced by these lavas falls in the "basic" or basalt (53.5 to 45% SiO₂) category. Several studies have shown that the mineral composition of basic lavas includes volcanic glass, basic plagioclases, small amounts of two pyroxenes, olivine, and little or no hornblende (Fieldes and Weatherhead, 1966; Mohr et al., 1972; and Tan, 1984; cited in Subagjo, 1988). In addition, small amounts of opaque minerals consisting of magnetite, titano-magnetite, and ilmenite are usually present (Subagjo, 1988).

Climate, especially soil moisture regime, is an important factor in formation of Andisols. This relationship was stressed by the work of Wright (1964) in South America. Working with two groups of soils, one from the high latitudes of Chile and Argentina, and another from the low latitudes of Ecuador and Colombia, Wright was able to correlate the soil moisture regime with minor

variations in soil morphology and with land use properties (cited in Wada, 1985).

Andisols commonly form under humid to perhumid conditions. It is possible that Andisols have formed under subhumid to arid climates or climates with pronounced dry seasons (Wada, 1985). Reports from workers in Kenya, Sudan, Rwanda, and Tanzania indicate that the process of soil formation from volcanic ash and the nature and properties of the resulting soil are distinctly different from those of Andisols formed in humid to perhumid climates (Wielemaker and Wakatsuki, 1984, cited in Wada, 1985).

Accumulation of organic matter, complexed with Al, is characteristic of Andisols in some regimes (Leamy, 1988). The characteristics of the organic matter in Hawaiian soils, and their variation with climate, have been extensively researched. In the subhumid to perhumid regions of Hawaii, the C content of soils derived from volcanic ash ranges from 5 to 15 percent in the A horizon, and 0.5 to 7 percent in the B horizon (Sherman and Swindale, 1964). Humus in Andisols is generally characterized by a wide C:N ratio, commonly with values over 13 (Wada, 1985). In comparison, C:N ratios of 10 to 11, and 14, were found in volcanic ash-derived soils in the subhumid and perhumid regions of Hawaii (Sherman and Swindale, 1964). The ratio of humic acid C to fulvic acid

C (Ch/Cf), an indicator of the extent of organic matter decomposition, also varies with climate. In humid (annual rainfall of 1800 to 5000 mm) regions, Ch/Cf is less than 0.5, while in subhumid to dry (annual rainfall of 600 to 2300 mm) regions, the Ch/Cf is greater than 0.5 (Arai, 1983, cited in Wada, 1985). Low Ch/Cf ratios indicate a lesser degree of humification and are characteristic of the fulvic Andisols (Ottawa et al., 1988). The amount, C:N ratio, and the form of humus are not affected by the petrographic nature of the parent volcanic ash (Wada, 1985).

Pedogenic Processes

Mineral weathering and transformation are the dominant pedogenic processes involved in formation of Andisols. By these processes, volcanic ash or other volcanoclastic parent material is metamorphosed, resulting in formation of weathering products. Extensive investigations of Andisols have revealed that the weathering products are short-range-order minerals, principally allophane, allophane-like constituents, imogolite and opaline silica (Wada, 1985). Sesquioxides, which usually occur as Al- and Fe- humus complexes and free Al, Fe- hydroxides, are present in considerable amounts (Subagjo, 1988). Noncrystalline Fe hydroxides, which may or may not be ferrihydrite, may also contribute

to andic properties (Leamy, 1987). Under some conditions, crystalline minerals such as halloysite and 2:1 and 2:1:1 layer silicates may be found (Wada, 1985, 1989).

Both allophane and imogolite have been observed in well-weathered volcanic ashes in Maui, Hawaii, an occurrence which indicates their stability under ustic moisture and isomesic temperature regimes (Wada et al., 1986, cited in Wada, 1989). The simultaneous availability of Si and Al appears to be essential for formation of these minerals.

Research has shown that accumulated humus plays a significant role in the transformation of primary minerals in volcanic ash parent material to short-range-order minerals, especially allophane and imogolite. This impact is directly related to the mechanism by which humus is accumulated in surface soil horizons.

It was first hypothesized that an interaction between allophane and humus protected the humus against the attack of microorganisms, thus allowing humus accumulation. This hypothesis implicitly assumes the preformation of allophane and related minerals. The results of several studies (i.e., Kato, 1970; Tokashiki and Wada, 1975; Inoue and Huang, 1987), however, support the hypothesis that the strong complexation of Al with humus limits the possibility of coprecipitation of Al and Si released from parent materials by weathering. The competition for the

released Al inhibits the formation of allophane and imogolite. A recent study indicates that climate has no significant impact on the inhibition process (Inoue and Higashi, 1988). In addition, the limitation of coprecipitation favors the formation of opaline silica (Wada, 1989).

Several other factors are also important in the formation of allophane and imogolite. Rainfall and vegetation influence formation of allophane and imogolite via the effect of these factors on soil pH (H_2O). Formation appears to be favored in horizons with pH (H_2O) values greater than 5.0 (Shoji et al., 1982). Nearly all varieties of volcanic ash (basaltic, andesitic, dacitic, or rhyolitic) produce allophane by weathering (Wada and Harward, 1974). Imogolite is usually associated with allophane produced in this manner (Wada, 1985). A thin (1 to 2 m) depositional overburden of volcanic ejecta, which serves as a silica source, also appears to favor formation of allophane and imogolite (Wada, 1989). Allophane-like constituents typically coexist with allophane and imogolite under these conditions. Imogolite may be formed either by transformation from allophane through desilication (i.e., increased leaching), or by precipitation from weathering solutions.

Ashes of various compositions may give rise to halloysite, which usually appears as unique spherical

particles with diameters of 0.04 to 1 micron (Wada, 1989). The amount of coexisting allophane increases as the particle size of the halloysite decreases. The relatively short life of allophane, allophane-like constituents, and imogolite in a leaching environment under warm, humid climates is indicated from its transformation to halloysite in old and buried soils (Wada, 1985). Halloysite-containing ash deposits from 10,000 to 250,000 years old have been reported (Wada, 1985).

The transformation of allophane and associated minerals to halloysite or gibbsite depends on whether the environment favors resilication or desilication. Where Si content in solution is likely to be low, through leaching and free drainage, allophane predominates. In cases where Si content in solution is likely to be high, through poor drainage or summer moisture deficit or with larger pumice grains, halloysite becomes the major component of the clay (Subagjo, 1988). The Si-rich environment produced by a thick depositional ash overburden favors resilication of allophane and the formation of halloysite (Wada, 1985).

Many Andisols contain 2:1 and 2:1:1 layer silicates, their intergrades and other mixed-layer minerals. Chlorite was found in soils derived from "tephric loess" in New Zealand (Wada, 1985). Soils containing a large amount of the layer silicates are derived from rhyolitic, dacitic, and andesitic ashes but not from basaltic-

andesitic and basaltic ashes (Shoji, 1983), which are the parent material of most Hawaiian Andisols. Layer silicates may be present as a result of input material from wind-blown dust or aeolian loess. Tropospherically derived quartz and micaceous vermiculite have been identified in soils of the Hawaiian islands (Jackson et al., 1971). The presence of non-pedogenic mica has been attributed to deposition of this quartz (Swindale and Uehara, 1966).

Opaline silica is most often found in the humus-rich surface and buried A1 horizons of younger soils (Subagjo, 1988). This mode of occurrence suggests that opaline silica is a product of the early stage of weathering of volcanic ash. Active Al ion released from the weathering of ash is suppressed by formation of Al-humus complexes in surface horizons (Wada, 1985, 1989). This process implies that the formation of opaline silica and Al-humus complexes proceeds in parallel fashion but that the formation of opaline silica and that of allophane and imogolite are antagonistic (Yoshinaga, 1988). Although the actual mechanism of silica concentration and precipitation is not known (Wada, 1985), it appears that opaline silica is deposited when soil solutions become supersaturated with silica.

Fe in Andisols is present mostly as noncrystalline hydroxides and partly as Fe-humus complexes (Yoshinaga,

1988). Researchers differ as to whether the noncrystalline hydroxide is ferrihydrite ($\text{HFe}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$), a short-range-order mineral. Reports of its presence in Andisols are few (Parfitt and Childs, 1983; Wada et al., 1986). Fe oxides are common in Andisols although approximately 90 percent of Andisols in the ICOMAND Andisol Database have less than 5 percent ferrihydrite (Parfitt, 1988).

APPENDIX 4

PEDOGENESIS OF OXISOLS

The major pedogenic processes in development of the oxic horizon are desilication and ferritization (van Wambeke et al., 1983).

Desilication is the loss of silica from the soil system through leaching. Silica and bases are preferentially soluviated, leaving behind Fe, Al, and Ti to form oxides and to undergo mineral transformations to form minerals such as kaolinite, gibbsite, hematite, goethite, and anatase (Fanning and Fanning, 1989). Most of this loss occurs "in the first flush of decomposition in the weathering crust near or at the rock surface in the initial material," (Cady, 1961). Further desilication of the soil material during erosional transport from soil profile to profile over vast expanses of time is usually involved in the genesis of Oxisols formed on transported parent materials (Buol et al., 1980).

Ferritization is the accumulation of iron as the net result of desilication. Addition of transported iron, probably in the ferrous form, followed by oxidation and precipitation, produce and iron "oxide" enriched material (Fanning and Fanning, 1989).

The processes of desilication and ferritization are possibly still active but had the most influence during the

alteration of materials prior to present soil pedon position. The combination of these two processes creates the low activity clay and the almost complete decomposition of weatherable primary minerals and 2:1 clay minerals (except Al-interlayered 2:1 and 2:2 intergradational minerals) required for the Oxisol order (van Wambeke et al., 1983). Both processes occur under oxidized, well-drained conditions.

Reducing conditions will further alter material by solubilizing iron. A fluctuating water table relatively near the surface at any time in the present or the past, leads to segregation of iron with some translocation to form the red-and-gray mottled soft material called plinthite. Large amounts of accumulated plinthite tend to form a continuous phase in the soil. If this material is subjected to repeated wetting and drying, as in exposure by overlying material, it becomes indurated to ironstone or beds of irregular nodular aggregates (Buol et al., 1980). The process leading to the formation of plinthite and ironstone have been termed "lateritization" (Fanning and Fanning, 1989).

Minerals such as kaolinite, gibbsite, goethite, hematite, and ferrihydrite as well as low amounts of anatase and rutile are formed as a result of transformations of primary and secondary minerals during soil development. For example, primary muscovite may be altered to secondary

aluminous chlorite (van Wambeke et al., 1983). In addition, secondary minerals which formed at an early stage, such as smectite and halloysite, may be destroyed or altered.

Kaolinite is one of the most commonly occurring clay minerals in soils, especially those of warm, moist climates. The widespread occurrence of kaolinite is due partially to its formation from many different minerals. For example, Garrels and Christ (1965) have shown that the stability field of kaolinite is bounded by those of gibbsite, K-mica, K-feldspar, and amorphous silica. Almost all primary silicate minerals, however, including biotite in recent years, have been listed as precursor minerals of kaolinite (Allen and Hajek, 1988).

Kaolinite formation is favored in the humid tropics with alternate wet and dry seasons and in well-drained areas of the landscape. Most kaolinite in soil parent materials originated by weathering in near-surface environments, but it may have been subjected to one or more sedimentary cycles subsequent to its original formation. Deeply weathered rock (saprolite) underlying Oxisols and Ultisols is commonly dominated by kaolinite (Allen and Hajek, 1989).

The clay weathering process leading to formation of kaolinite in the Molokai series has been described as follows: "As rocks weather, montmorillonite clay forms in 'pockets' in the interior of the rocks where the bases are still high. Secondary micas that give dehydration curves

like vermiculite also form in the interiors of the weathering rocks. Immediately below basalt rocks in the soil there is often an area high in montmorillonite clay. As the bases are depleted, the montmorillonite breaks down so the resulting Low Humic Latosol (Oxisol) is high in kaolinite," (Johnson, 1956).

Distribution of kaolinite with profile depth is remarkably uniform. Often, however, less kaolinite has been reported in the upper solum than in the lower solum and substratum (Allen and Hajek, 1989).

Gibbsite, $\text{Al}(\text{OH})_3$ is by far the most common Al hydroxide in soils; it is often the predominant mineral in the clay fraction. Gibbsite seems to form mostly in well-drained soils such as Udox, and in warm climates, but it has been listed as a significant component in Ustox (Allen and Hajek, 1989). The results of laboratory studies suggest that rapid precipitation usually yields one or both of the other $\text{Al}(\text{OH})_3$ polymorphs, bayerite or nordstrandite, whereas slow crystallization yields gibbsite. The rate of formation of $\text{Al}(\text{OH})_3$ in the soil environment is slow and favors the development of gibbsite, thus confirming the laboratory results (Hsu, 1989).

The primary aluminum silicates in igneous rocks are high-temperature products, and are not stable under present environments (Hsu, 1989). Under favorable conditions, those primary aluminum silicates eventually will weather to

$\text{Al}(\text{OH})_3$. In his studies under humid tropical climates, Harrison (1934) found that basic or intermediate rocks weathered directly to gibbsite, but acidic rocks weathered through kaolinite to gibbsite. Basic rocks contain Al-rich feldspathoids and plagioclase which are highly susceptible to chemical weathering. In addition, basic rocks contain ferromagnesian minerals such as olivine and pyroxene; these minerals are usually the first constituents to decompose in chemical weathering. The decomposition of these mineral yields a porous texture providing conditions for good drainage (Hsu, 1989).

Gibbsite and the various polymorphs of FeOOH and Fe_2O_3 commonly exist together as the end products of advanced weathering. In general, Fe_2O_3 and FeOOH appear earlier and more often than gibbsite in the process of soil genesis (Hsu, 1989).

The usual pathway proposed for gibbsite formation is by the desilication of kaolinite. It has been reported that the proportions of kaolinite and gibbsite are frequently inversely related, with gibbsite the dominant mineral in highly weathered soils and kaolinite the dominant mineral in less weathered ones (Hsu, 1989).

Two additional mechanisms for the genesis of gibbsite have been proposed. The first hypothesis proposes that primary aluminum silicates weather directly to gibbsite (e.g., Sherman et al., 1967). The second hypothesis

proposes that the primary aluminum silicates weather to clay mineral intermediates, which in turn weather to gibbsite. For example, Bates (1962) presented evidence showing the feldspar-halloysite-gibbsite transition in the weathering of andesites in Hawaii. In the least weathered of these specimens, halloysites appeared along with unaltered feldspar, while in the more weathered specimens, halloysite became dominant, accompanied by the destruction of feldspar and the appearance of gibbsite. Gibbsite and iron oxides were abundant in highly weathered specimens.

The two mechanisms are not mutually exclusive nor totally independent. The initial step of chemical weathering of primary minerals involves the displacement of the balancing bases with H^+ . This disturbance of the soil system is followed by the breakdown of Al-O-Si linkages, releasing Al and Si to solution. Once Si is separated from Al, the gibbsite formation can occur very rapidly (Hsu, 1989). If the percolating water moves slowly, its Si concentration may gradually increase and recombine with Al to form kaolinite (Kittrick, 1970). Whether the primary Al silicates weather directly to gibbsite or through a kaolinite intermediate is governed by the intensity of leaching. Leaching intensity is in turn affected by a number of factors such as rainfall, temperature, parent material, topography, ground-water table, vegetation and time (Hsu, 1989).

All of the studies which show evidence for direct gibbsite formation were conducted under conditions of high rainfall, tropical or subtropical temperature, basic or intermediate rocks, and upland; in other words, an environment of excessive drainage existed in each case (Hsu, 1989). In contrast, the presence of a kaolinite intermediate was observed under conditions where the drainage condition is only moderate (Hsu, 1989).

The previous discussion assumes that kaolinite is the sole product of Al-Si interaction. The reaction products of this interaction may also include amorphous Al silicates of varying composition, allophane, halloysite, and other similar minerals. Although such components are not stable (Hsu, 1989), they could be significant in less weathered soils. For example, gibbsite has been identified in such immature soils as Andepts, which frequently have allophanic mineralogy. This apparently anomalous occurrence of gibbsite is usually ascribed to the rapid desilication that takes place in very permeable materials under high rainfall (Allen and Hajek, 1989).

Similarly, released Al may react with other soil constituents, such as particles of partially altered parent materials, sulfate, phosphate, or organic matter to form a variety of transition products. The formation of these intermediates may account for the slow crystallization of

gibbsite in some young soils, especially those soils with poor drainage conditions (Hsu, 1989).

Further erosional activity cannot be ignored as a factor in the Al-Si interaction. Although kaolinite will desilicate to gibbsite under continual leaching, the possibility that the clay minerals may be transferred and redeposited elsewhere does exist.

Finally, gibbsite may form directly from primary micaceous minerals. Micromorphological evidence from numerous studies indicate that gibbsite often forms pseudomorphically after feldspars; moreover, gibbsite formation after biotite has been reported (Allen and Hajek, 1989). A weathering sequence which represents a continual process of desilication as suggested by Jackson, (1964), is widely accepted. This sequence proposes that mica weathers first to vermiculite, then to smectite, to OH-Al interlayered smectite, to kaolinite, and eventually to gibbsite.

Goethite (α FeOOH) is generally considered the most widespread Fe mineral in soils (Schwertmann and Taylor, 1989). Goethite tends to impart yellowish brown to brown colors to soils, and forms exceedingly small particles (Allen and Hajek, 1989).

Iron released during weathering of Fe-bearing primary minerals serves as the Fe source for much of the goethite formed (Allen and Hajek, 1989). Under specified conditions,

goethite may also form from ferrihydrite ($\text{HFe}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$) (Allen and Hajek, 1989).

Goethite occurs under a wide range of climatic conditions. The proportion of goethite to hematite ($\alpha\text{Fe}_2\text{O}_3$) seems to be higher in soils of cool temperate and cold regions than in warm temperate and tropical regions (Schwertmann and Taylor, 1989), yet it is a significant component of most Oxisols. Its formation seems to be favored by wetter soil conditions (Allen and Hajek, 1989).

In keeping with the central concepts of the Oxisol order, it cannot be assumed that all the goethite in soils was formed in the pedogenic environment which currently prevails. Much of it may have been inherited from transported sediments. Ultimately, however, gibbsite formation must have occurred in near-surface environments (Allen and Hajek, 1989).

The amount of Al substitution in the goethite structure is often considerable, sometimes as much as 30 mole percent (Schwertmann and Taylor, 1989) and may prevail in tropical and subtropical climates. Several studies have observed higher Al substitution in goethites from highly weathered tropical and subtropical soils, bauxites, and saprolites (Bigham et al., 1978; Schwertmann and Kampf, 1984, cited in Schwertmann and Taylor, 1989).

The factors determining the degree of Al substitution in goethite are not yet fully understood. The activity of

soluble Al in the environment of the developing goethite crystals may be an important factors, and can be influenced by pH and Si concentration (Schwertmann and Taylor, 1989). This may explain why goethites in gibbsitic, highly desilicified environments often are highly Al-substituted (Schwertmann and Taylor, 1989). In addition, pedogenic environments characterized by high Al and low Si activity favor both goethite and hematite with high Al substitution (Schwertmann and Kampf, 1985). Thus, the two minerals often occur together (Allen and Hajek, 1989).

Hematite (α Fe₂O₃) is a significant authigenic component of the clay fraction in most well-drained Oxisols and Ultisols (Allen and Hajek, 1989). Like goethite, hematite forms extremely small crystallites (Allen and Hajek, 1989).

The name hematite refers to the bright red color of the mineral when in this finely dispersed state. This distinctive color makes hematitic soils red (5YR and redder); the redness of various soils has been found to be significantly correlated with their hematite content (Schwertmann and Taylor, 1989). Because of its greater pigmenting power, hematite can mask the yellow to yellow-brown color of higher concentrations of goethite. For example, goethite in "red podzolic" Australian soils was reported to be masked by hematite (Davey et al., 1975, cited in Allen and Hajek, 1989).

Synthetic hematite crystals produced at near-pedogenic conditions generally exhibit a hexagonal morphology. This morphology is usually less well expressed by soil hematites. In soils where goethite and hematite coexist, the hematite crystals often, but not always, are larger, thus presenting a correspondingly smaller specific surface (Schwertmann and Taylor, 1989).

Hematite is more abundant in soils of tropical and warm temperate regions than in colder areas, and is more widespread in well-drained soils than in associated soils with restricted drainage. The more rapid decomposition of organic matter in the warmer and/or better-drained soils may influence these relationships.

Ferrihydrite ($\text{HFe}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$) is a poorly ordered Fe^{3+} oxide previously referred to as "amorphous ferric hydroxide," (Schwertmann and Taylor, 1989). X-ray and electron diffraction analyses and IR spectroscopy, however, have shown that ferrihydrite has short-range-ordering leading to broad XRD lines and that it is not a true hydroxide (Schwertmann and Taylor, 1989).

Ferrihydrite is a widespread and characteristic component of young Fe-oxide accumulations. Its color is more reddish than goethite but less red than hematite (Schwertmann and Taylor, 1989). This mineral is an important supplier of Fe for goethite and gibbsite formation.

Although goethite is the most widespread Fe oxide in soils and mineral weathering environments, it is frequently associated with hematite, especially in warmer areas. This association is a very common feature in the majority of soils of the tropical and subtropical regions (Schwertmann and Taylor, 1989).

Among pedoenviromental factors influencing the goethite:hematite ratio are the initial valence of the Fe source (divalent or trivalent), its concentration in solution, and parameters such as pH, Eh, temperature, soil water activity, soil organic matter, activity of Al in the soil solution, and the ionic environment (Schwertmann and Taylor, 1989).

Within the pH range of 4 to 6, a negative correlation between soil pH and the goethite:hematite ratio was found in some soils of south Brazil. Laboratory results are in agreement with this field observation. Ferrihydrite was converted to goethite and hematite in vitro at constant room temperature but at various pHs. A goethite maximum was obtained around pH 4 and a maximum of hematite (minimum of goethite) was obtained at pH 7 to 8 (Schwertmann and Taylor, 1989).

The hematite:goethite ratio usually increases with increasing soil temperature (Schwertmann and Taylor, 1989). This ratio may also be influenced by the soil moisture activity. For example, the soil moisture activity may have

been responsible for variations in the relative proportions of hematite and goethite along a 176-meter toposequence of Oxisols in Central Brazil (Schwertmann and Taylor, 1989).

Schertmann and Taylor (1989; page 399) illustrate a model which describes formation and transformation of the various iron oxide minerals, including goethite, hematite and ferrihydrite. In this model, formation and transformation occur through two mutually competitive pathways, with ferrihydrite as a significant intermediate.

According to the model, goethite is formed via solution, through nucleation and crystal growth, preferentially utilizing the monomeric, monovalent Fe^{3+} ions, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-$. These monomers may be supplied by any Fe source (including ferrihydrite) under suitable conditions.

In contrast, hematite forms from ferrihydrite or its precursors through aggregation, dehydration, and internal structure rearrangement of the minute ferrihydrite particles. This process is suggested by the similarity between the structures of ferrihydrite, which possesses a hematite-type structure, and hematite. Ferrihydrite differs from hematite in that it is highly disordered and contains water. Ferrihydrite is now considered a necessary precursor of hematite (Schwertmann and Taylor, 1989).

Schwertmann and Taylor (1989) assert that factors which favor the formation of ferrihydrite and its aggregation,

dehydration, and structural rearrangement necessarily also favor hematite formation at the expense of goethite. Soil temperature and water activity act directly on the dehydration and rearrangement of ferrihydrite to yield hematite.

Soil pH, organic matter, and rate of Fe release are important factors influencing the ferrihydrite-hematite-goethite association. The interaction between these factors is complex. As the soil pH rises from 4 to 8, the activity of the $\text{Fe}(\text{OH})_2^+$ ion decreases and the rate of goethite formation is reduced (Schwertmann and Taylor, 1989). On the other hand, if relatively stable Fe-organic complexes are formed, as in cool and wet climates, Fe^{3+} is slowly released. In this case, the possibility of exceeding the solubility product of ferrihydrite is reduced and hematite formation is inhibited (Schwertmann and Taylor, 1989). Instead, goethite formation is favored as nuclei can form from the liberated soluble $\text{Fe}(\text{OH})_2^+$ species.

Alternatively, if the rate of Fe release from the source is increased, or if the breakdown of Fe organic complexes is accelerated, as under hot and dry conditions, the probability of exceeding the solubility product of ferrihydrite increases. Once formed, ferrihydrite can act as a source of Fe for formation of hematite as well as goethite. In general, therefore, hematite and goethite form

via two mutually competitive processes involving ferrihydrite (Schwertmann and Taylor, 1989).

Certain minor processes may be involved in the formation of specific groups of Oxisols. Melanization and humification occur in all Oxisols to some degree, although it is especially evident in soils of the Humox suborder. The high biomass resulting from the higher solar radiation and year-round warm temperature of tropical climates humifies and mineralizes rapidly. A high equilibrium level of organic matter, however, is maintained (Sanchez and Buol, 1975 cited in Buol et al., 1980). These processes are also active in Oxisols with high rainfall and that are usually moist.

Gleization, the wetness-induced reduction of iron (Fanning and Fanning, 1989), may be a major process in Oxisols that are or have been saturated with water at some period or periods during the year (Buol et al., 1980). This process does not necessarily cause the formation of plinthite.

Pedoturbation, either by plant roots or by animal activities, will be an active process if there is no continuous plinthite very near the surface. Pedoturbation may also occur if there is no currently active gleization, with its associated high water table. The primary cause of faunal pedoturbation is termites (Buol et al., 1980).

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